การใช้สารผสมระหว่างสารลดแรงตึงผิวประจุบวกและประจุลบในการฟื้นฟูชั้นดินที่ปนเปื้อนสไตรีนและเอธิลไซโคลเฮ็กเซน

นางอรัญญา เฟื่องสวัสดิ์

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UTILIZATION OF MIXED ANIONIC/CATIONIC SURFACTANTS FOR STYRENE AND ETYHLCYCLOHEXANE SOLUBILIZATION/ENTRAPMENT IN CONTAMINATED SUBSURFACE REMEDIATION TECHNOLOGIES

Mrs. Aranya Fuangswasdi

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By	Mrs. Aranya Fuangswasdi
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Thesis Advisor	Professor David A. Sabatini, Ph.D.
Thesis Co-Advisor	Khemarath Osathaphan, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Degree of Doctor

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(Assistant Professor M.R. Kalaya Tingsabadh, Ph.D.)

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อรัญญา เฟื่องสวัสดิ์: การใช้สารผสมระหว่างสารลดแรงตึงผิวประจุบวกและประจุลบในการฟื้นฟูชั้นดินที่ปนเปื้อนสไตรีนและเอธิลไซโคลเฮ็กเซน (UTILIZATION OF MIXED ANIONIC/CATIONIC SURFACTANTS FOR STYRENE AND ETHYLCYCLOHEXANE SOLUBILIZATION / ENTRAPMENT IN CONTAMINATED SUBSURFACE REMEDIATION TECHNOLOGIES) อ. ที่ปรึกษา : Prof. Dr. David A. Sabatini อ. ที่ปรึกษาร่วม ดร. เขมรัฐ โอสถาพันธุ์ 121 หน้า ISBN 974-53-2386-1

งานวิจัยนี้เป็นการศึกษาการใช้สารผสมของสารลดแรงตึงผิวประจุบวกและประจุลบ โดยการคัดเลือกสารลดแรงตึงผิวชนิดประจุบวกและประจุลบสองคู่ ได้แก่ 1) สารลดแรงตึงผิวประจุบวกชนิดสองหัวหนึ่งหาง คือ pentamethyl-octadecyl-1,3-propane diammonium dichloride (PODD) ซึ่งเป็นส่วนผสมหลัก ผสมกับสารลดแรงตึงผิวประจุลบชนิดหนึ่งหัวหนึ่งหาง คือ sodium dodecyl sulfate (SDS) นำมาวิจัยการดูดซับบนซิลิกาซึ่งเป็นประจุลบ และ 2) สารลดแรงตึงผิวประจุลบชนิดสองหัวสองหาง คือ sodium hexadecyl-diphenyloxide disulfonate (SHDPDS) ซึ่งเป็นส่วนผสมหลัก ผสมกับสารลดแรงตึงผิวประจุบวกชนิดหนึ่งหัวหนึ่งหาง คือ dodecylpyridinium chloride (DPCl) นำมาวิจัยการดูดซับบนอะลูมินาซึ่งเป็นประจุบวก

ผลการวิจัยการดูดซับ (Adsorption) พบว่า สารผสม SDS/PODD ในอัตราส่วน 1 ต่อ 3 มีประสิทธิภาพในการดูดซับบนพื้นผิวของซิลิกาดีที่สุด และไม่ก่อให้เกิดการตกตะกอนของสารผสมของสารลดแรงตึงผิว ส่วนสารผสม SHDPDS/DPCl มีอัตราการดูดซับบนพื้นผิวของอะลูมินาเกือบเท่า ๆ กันในหลายอัตราส่วน และ ใน SHDPDS เพียงอย่างเดียว

ผลการวิจัยการดูดซึมน้ำมันของสารลดแรงตึงผิว (Solubilization) และการนำเอาสารดูดซับไปดูดซึมน้ำมัน (Adsolubilization) พบว่าสารผสม SDS/PODD ในอัตราส่วน 1 ต่อ 3 สามารถดูดซึมสไตรีนและเอธิลไซโคลเฮ็กเซน ได้ดีกว่าสารผสมในอัตราส่วนอื่น ๆ ในขณะที่สารผสม SHDPDS/DPCl มีอัตราการดูดซึมน้ำมันไม่แตกต่างกันในหลายอัตราส่วน

การนำเอาสารดูดซับซิลิกาที่มีสารผสม SDS/PODD ในอัตราส่วน 1 ต่อ 3 ดูดซับอยู่บนพื้นผิวมาทำการวิจัยการชะลอการเคลื่อนที่ของน้ำมัน พบว่า สารดูดซับดังกล่าวสามารถชะลอการเคลื่อนที่ของสไตรีนได้มากกว่าการเคลื่อนที่ปกติถึง 12.8 เท่า และชะลอการเคลื่อนที่ของเอธิลไซโคลเฮ็กเซนได้มากกว่าการเคลื่อนที่ปกติถึง 90.2 เท่า

สาขาวิชาการจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต..
(สาขาวิชา) ลายมือชื่ออาจารย์ที่ปรึกษา ....
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ARANYA FUANGSWASDI: UTILIZATION OF MIXED ANIONIC/ CATIONIC SURFACTANTS FOR STYRENE AND ETYHLCYCLOHEXANE SOLUBILIZATION/ENTRAPMENT IN CONTAMINATED SUBSURFACE REMEDIATION TECHNOLOGIES. THESIS ADVISOR: PROF. DAVID A. SABATINI, PH.D., THESIS CO-ADVISOR: KHEMARATH OSATHAPHAN, PH.D.121 pp. ISBN 974-53-2386-1

This research reports the studies of mixtures of anionic and cationic surfactants having single and twin head groups. The surfactant mixtures investigated were: (a) a single-head anionic surfactant, sodium dodecyl sulfate (SDS), in mixture with the twin-head cationic surfactant pentamethyl-octadecyl-1,3-propane diammonium dichloride (PODD) - adsorption was studied on silica; and (b) a twin-head anionic surfactant, sodium hexadecyl-diphenyloxide disulfonate (SHDPDS), and the single-head cationic surfactant dodecylpyridinium chloride (DPCl) - adsorption was studied on alumina. While the mixed surfactant system of SHDPDS/DPCl showed comparable adsorption on alumina to SHDPDS-alone, the mixed surfactant system of SDS/PODD showed increased adsorption on silica as compared to PODD-alone.

Mixtures of SDS/PODD showed solubilization synergism when mixed at a molar ratio of 1:3; however, solubilization experiments of mixed SHDPDS/DPCl at a ratio of 3:1 did not show solubilization enhancement over SHDPDS-alone. The adsolubilization of ethylcyclohexane was greater in mixed SDS/PODD system than for PODD-alone and in mixed SHDPDS/DPCl system than for SHDPDS-alone.

The experiments of organic solutes retardation through the column packed with silica adsorbent showed dramatical synergism of mixed surfactant which adsorbed on silica surface. Thus this study suggests that the adsorbent of mixed admicelles on silica can be effectively used for groundwater plume management without the contamination from the surfactants themselves.

Inter-department Environment Management Student's signature..........................
Field of Study Environment Management Advisor's signature..........................
Academic year 2006 Co-Advisor's signature..........................

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ABBREVIATIONS

μL	Micro liter
°C	Degree celcius
AIS	Anionic surfactant
Al_2O_3	Alumina
A_{min}	Minimum coverage area
C14	Carbon 14
C14-1	Carbon 14-1
C16-1	Carbon 16-1
C18	Carbon 18
C18-1	Carbon 18-1
C18-2	Carbon 18-2
CIS	Cationic surfactant
cm	Centimeter
CMC	Critical micelle concentration
DPCl	Dodecylpyridinium chloride
FID	Flame ionization detector
FIG	Figure
GC	Gas Chromatograph
HCl	Hydrochloric
HPLC	High performance liquid chromatography
L	Liter
M	Molar
M/M	Molar per molar

m^2/g	Square meter per gram
mL	Milliliter
mL/min	Milliliter per minute
mM	Millimolar
mmole/L	Millimole per liter
mN/m	Millinewton per meter
MSR	Molar solubilization ratio
N/A	Not available
NaCl	Sodium chloride
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
NAPL	Nonaqueous-phase liquid
NM	Not measurable
nm^2	Nanometer square
PODD	Pentamethyl-octadecyl-1,3-propane diammonium dichloride
R	Retardation
rpm	Round per minute
SDHS	Sodium dihexyl sulfosuccinate
SDS	Sodium dodecyl sulfate
SHDPDS	Hexadecyl-diphenyloxide disulfonate
SiO_2	Silica
UV	Ultraviolet
VIS	Visible

CHAPTER I

INTRODUCTION

1.1 General

The use of surfactants in subsurface remediation has been evaluated for many years (Harwell et al., 1999). The economics of surfactant-enhanced subsurface remediation are affected by the losses of surfactants due to precipitation, sorption, and other phenomena. Single surfactant systems using either ionic or nonionic surfactants have been used in remediation of organic contamination with moderate success. Appropriate anionic/cationic mixtures are expected to enhance the remediation of subsurface by increasing the solubilization/adsorption capacity of mixed surfactant micelles and admicelles. In order to take advantage of the synergism of anionic/cationic surfactant mixtures, the adsorption of mixed anionic and cationic surfactants on silica and alumina is studied. Later these adsorbed mixed surfactant phases (anionic/cationic admicelles) will be used to design subsurface barriers to trap or retard the spread of organic contaminant plumes in aquifer media.

1.2 Hypotheses

First, we hypothesize that by using mixtures of anionic and cationic surfactants we will observe a synergistic adsorptive behavior as evidenced by having higher surfactant adsorption at sub-CMC surfactant concentrations and by reaching the adsorption plateau (Region IV) at lower surfactant concentrations compared to single surfactant systems; this hypothesis is based on the lower CMC observed for mixtures of anionic and cationic surfactants compared to mixtures of similarly structured surfactants.

The second hypothesis is that an increased level of plateau surfactant adsorption will result because of the tighter packing density in adsorbed aggregates of these mixed surfactants due to reduction in charge repulsion between adjacent adsorbed surfactants compared to single surfactant systems.

The third hypothesis is that by introducing mixtures of anionic and cationic surfactants it is possible to improve the solubilization capacity of micelles and admicelles, and that this effect will depend on the mole ratios of mixed admicelles and the polarity/hydrophobicity of the solute.

The last hypothesis is that the adsorbent with mixed adsorbed surfactant will cause more retardation of styrene and ethylcyclohexane than the adsorbent without admicelles, and with surfactant-alone. It is also hypothesized that, due to the lower CMC, the stability of the mixed surfactant admicelles on the adsorbent will be greater than for the single surfactant system.

1.3 Objectives of the study

The main goals of this work are to evaluate synergism of surfactant adsorption onto solid surfaces by using anionic and cationic surfactant mixtures, and to determine how properties of these adsorbed mixtures impact the co-adsorption or adsolubilization of different types of solutes. While of secondary interest, we will also evaluate the precipitation of anionic/cationic surfactant mixtures to define isotropic concentration regimes in which to conduct the adsorption studies.

The third objective of this study is to evaluate the solubilization capacity of micelles and admicelles formulated with mixtures of anionic and cationic surfactants as a function of anionic/cationic molar ratio, and to probe the internal environment of micelles and admicelles produced with these mixtures by using solutes of differing polarity.

The fourth objective of this work is to use column studies to build on results of batch studies using adsorbent with mixed admicelle surfactant as compared to the adsorbent without admicelle.

Finally, this research aims to investigate the structure of the admicelles by using microscope techniques in order to study and compare the size of the admicelles of surfactant-alone and mixed surfactants. The minimum coverage area of monolayer and bilayer of surfactants onto mineral oxide surface is also studied by using surface tension experiments.

1.4 Scope of the study

The research seeks to investigate how the composition of mixed anionic/cationic surfactant systems (AIS/CIS) impacts the adsorption of both surfactants onto negatively and positively charged solid media (silica and alumina respectively), in batch adsorption experiments and in continuous flow (column) experiments.

The adsorption isotherms and solubilization will be obtained and analyzed in terms of the CMC of the mixture and compared to the behavior of single surfactant systems to identify evidence of synergism.

The adsolubilization of styrene and ethylcyclohexane in mixed surfactant admicelles formed on the surface of silica and alumina will be studied. The retardation of the organic solutes and the mass balance of the organic solutes and the surfactant will be studied. The admicelle structure of mixed and single surfactants will be investigated.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

This chapter describes the theoretical background and provides a literature review on precipitation of mixed surfactant, surfactant adsorption, solubilization, adsolubilization of organic solutes, the column study, and electron microscope studies.

2.1 Precipitation of mixed surfactant

Mixtures of anionic and cationic surfactants have demonstrated synergistic behavior, as evidenced by ultralow critical micelle concentrations (CMCs), increased surface activity (Scamehorn, 1986a; Mehreteab, 1999) and improved detergency performance (Randal, 1993). The main disadvantage of mixed anionic and cationic surfactant systems is their tendency to form precipitate or liquid crystal phases (Scamehorn and Harwell 2005). Precipitation negatively impacts surfactant use in many applications, such as detergency performance and subsurface remediation of oil contamination (Harwell, 1992; Scamehorn and Harwell 2005).

To understand surfactant precipitation, it is helpful to recognize that at low concentrations, anionic and cationic surfactants exist as dissociated surfactant monomers. As the surfactant concentration increases, micelles begin forming at the critical micelle concentration or CMC (Rosen, 1989a; Scamehorn et al., 2004a). For anionic and cationic surfactant systems, when the monomer concentration equals or exceeds its solubility limit, precipitate will form (Scamehorn et al., 1986b). Below the CMC, all of the surfactants are present as monomers; and as the concentration of one of the surfactants increases, a lesser concentration of the oppositely charged surfactant is needed to cause precipitation. This equilibrium is modeled using the solubility product as shown in Equation 2-1 (Scamehorn et al., 1986b):

$$AC \Leftrightarrow A^- + C^+ \Rightarrow K_{sp} = [A^-][C^+] \qquad [2\text{-}1]$$

where A^- is the concentration of the anionic surfactant monomer, C^+ is the concentration of the cationic surfactant monomer, AC is the concentration of the precipitate, and K_{sp} is the concentration-based solubility product of the precipitate. Activity coefficients are omitted from Equation 2-1 since they vary little over the concentration range of interest and can be difficult to evaluate for micellar systems.

The monomers, precipitate and micelle phase boundaries for the surfactant mixtures hexadecyl-diphenyloxide disulfonate (SHDPDS) and dodecylpyridinium chloride (DPCl) and sodium dihexyl sulfosuccinate (SDHS) and already defined DPCl are presented in Figure 2-1. Three precipitation boundaries are apparent in Figure 2-1; the first one occurs at low concentrations of both surfactants and corresponds to the monomer-precipitate equilibrium described by Equation 2-1. The right-hand side of the phase boundary corresponds to the equilibrium between anionic-rich micelles and the precipitate. The left-hand phase boundary corresponds to the equilibrium between the cationic-rich micelles and the precipitate. The vertices of the phase diagram correspond to the critical micelle concentrations of the surfactant mixtures. By looking at the precipitation phase diagram in Figure 2-1, it is apparent that the precipitation region in the system SHDPDS/DPCl is smaller than the precipitation of the system SDHS/DPCl (Doan et al., 2003). Doan et al. (2003) suggested that the twin-head structure of SHDPDS caused it to resist precipitation and thus accounted

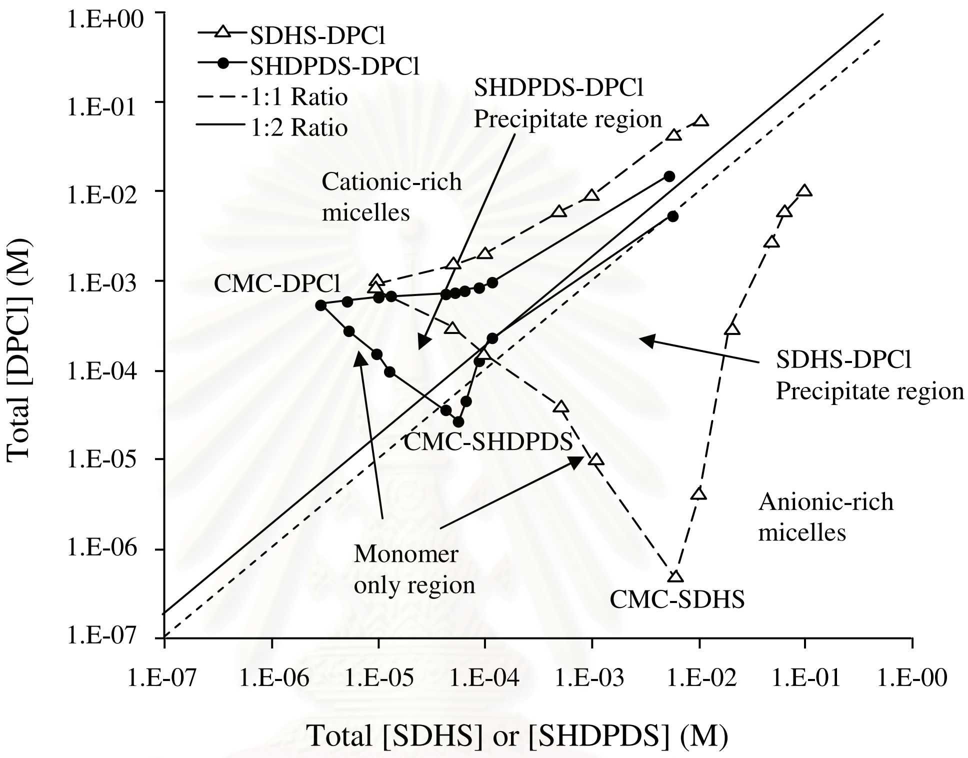


FIG. 2-1. Precipitation diagrams for mixed surfactant systems, sodium dihexyl sulfosuccinate and dodecylpyridinium chloride (SDHS/DPCl), and diphenyloxide disulfonate and dodecylpyridinium chloride (SHDPDS/DPCl), 0.15 M NaCl, 25°C. (Adapted from Doan et al., 2003).

for the smaller precipitation region. In this work we evaluate the precipitation of a twin-head cationic surfactant (pentamethyl-octadecyl-1,3-propane diammonium dichloride - PODD) with an oppositely charged and single-head anionic surfactant (sodium dodecyl sulfate - SDS); we expect that this combination will be more resistant to precipitation, and can thus be formulated over a wider range of concentrations than a combination of two oppositely-charged single-head surfactants (SDS/DPCl).

The ability to reduce the precipitation potential of anionic and cationic surfactant mixtures will allow exploitation of the potential synergism for these systems to produce ultra-low CMCs, to enhance oil solubilization and microemulsion formation and to enhance adsorption. In this research we are especially interested in the possibility of increasing the adsorption of surfactant mixtures onto mineral surfaces (silica and alumina) for use as adsorbent materials for organic molecules.

2.2 Adsorption isotherm

Figure 2-2 presents a typical adsorption isotherm of an ionic surfactant on an oppositely-charged mineral surface which can be divided into four regions (Scamehorn et al., 1982). At very low surfactant concentration (Region I or the Henry's Law region), the adsorption is proportional to surfactant concentration. In Region I, adsorption density is so low that no significant interaction between adsorbed molecules occurs. Region II is characterized by a rapid increase in adsorption due to tail-tail interactions and the onset of bilayer coverage or admicelle formation. In Region II, adsorption increases with concentration as successively less energetic patches fill with admicelles. In Region III, the adsorption increases more slowly with concentration than in Region II, likely due to lateral hindrances between adsorbed surfactants and heterogeneities in surface potentials. Region IV is the plateau adsorption region where adsorption is constant because the surfactant concentration exceeds the CMC.

From the adsorption experiments by solution depletion, the amount of the surfactant adsorbed onto silica and alumina surface is obtained by Equation 2-2 (Rosen, 1989b).

$$\Gamma = \frac{V_L(C_1 - C_2)}{m} \qquad [2\text{-}2]$$

where Γ is the adsorption of surfactant on the solid surface in mole/gram, V_L is the volume of the liquid phase in L, C_1 is the concentration of surfactant before adsorption in mole/L, C_2 is the concentration of surfactant at adsorption equilibrium in mole/L, and m is the mass of the adsorbent in gram. Alternatively, the adsorption can be expressed on a unit area basis (mole/m^2) by dividing Γ from Equation 2-2 by the adsorbent surface area (m^2/g).

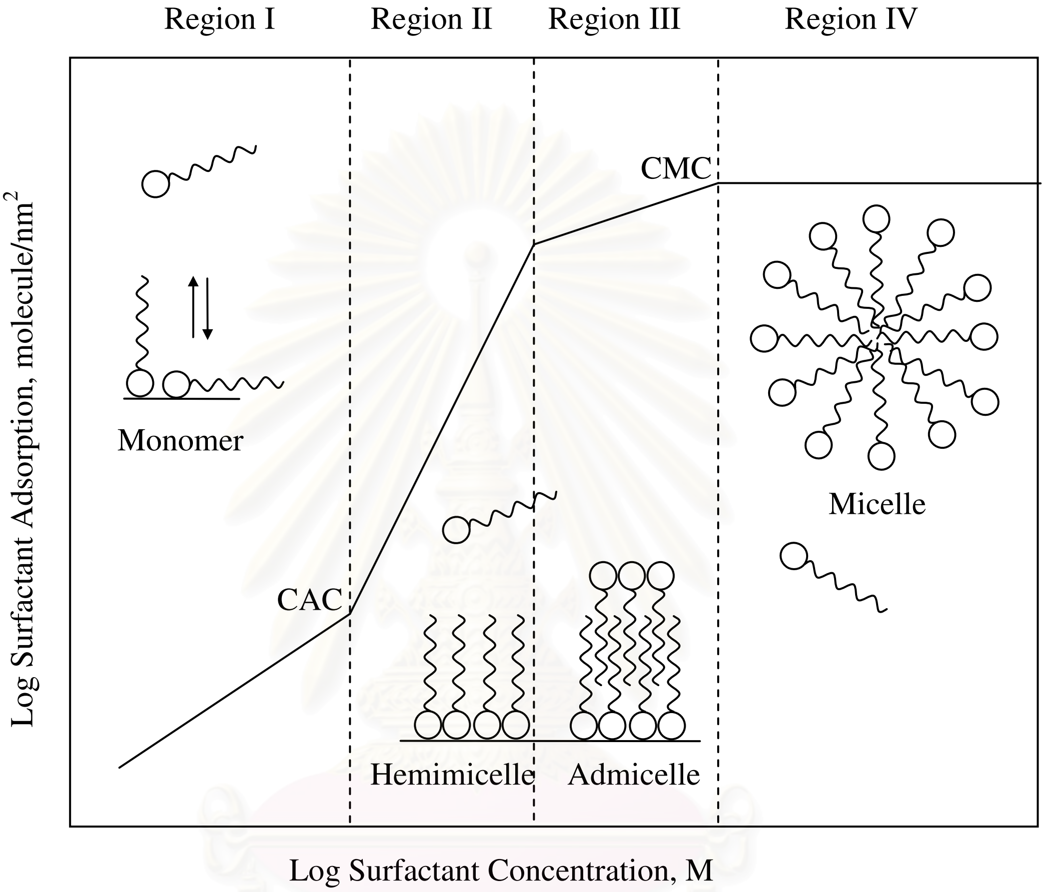


FIG. 2-2. Adsorption isotherm of a surfactant onto a solid surface (Modified from Scamehorn et al., 1982).

To date, only a limited number of adsorption studies have been conducted with mixtures of anionic and cationic surfactants due to precipitation limitations and analytical challenges (Marques et al., 1993; Li et al., 1996; Bergström 2001; Kang et al., 2001; Rodriguez et al., 2001; Chen et al., 2002) Thus, while adsorption is the primary focus of this research, we also conducted precipitation studies to indicate where we can conduct our adsorption studies and avoid precipitation. In this work we take advantage of the smaller precipitation region which results from using a combination of single-head and twin-head ionic surfactants, which results in a larger isotropic concentration regime in which adsorption can be studied (Doan et al., 2003).

2.3 Solubilization

Micelles are formed when the surfactant concentration exceeds the critical micelle concentration (CMC). Above the CMC, surfactant monomers associate with one another to form micelles which have a hydrophobic interior. When an oil phase is in contact with an aqueous micellar solution, oil molecules partition into the hydrophobic core of these micelles, a process known as solubilization (Rosen, 1989c; Broze, 1995; Scamehorn et al., 2004b). Solubilization is sometimes expressed as the amount of oil solubilized per mass, volume or moles of surfactant present in micelles at saturation (Rosen, 1989c) (Figure 2-3). Surfactant systems with higher solubilization capacities are desirable as they reduce surfactant requirements and formulation costs in applications such as surfactant-based separation processes, enhanced oil recovery and environmental remediation technologies (Harwell, 1992; Rouse et al., 1993; Sabatini et al., 2000).

The partition of various organic solutes into the micelle can be described by the micellar partition coefficient, K_{mic}, shown in Equation 2-3 (Rosen, 1989c; Edwards et al., 1991).

$$K_{mic} = \frac{X_{mic}}{X_{aq}} \qquad [2\text{-}3]$$

where X_{mic} is the mole fraction of the organic solute in the micelle pseudophase and X_{aq} is the mole fraction of organic solute in the aqueous phase. X_{mic} and X_{aq} are calculated by Equations 2-4 and 2-5, respectively (Rosen, 1989c; Edwards et al., 1991; Nayyar et al., 1994).

$$X_{mic} = \frac{MSR}{1 + MSR} \qquad [2\text{-}4]$$

$$X_{aq} = \frac{C_{eq}}{C_{eq} + 55.55} \qquad [2\text{-}5]$$

where the molar solubilization ratio (MSR) is the moles of the solute solubilized per mole of surfactant in micelles and is determined by the slope of the graph of surfactant concentration versus oil concentration in mole/L. C_{eq} is the equilibrium concentration of the organic solute in water alone and 55.55 is the inverse molar volume of water. In solubilization studies, C_{eq} is the water solubility concentration of the oil, as shown in Table 3-2.

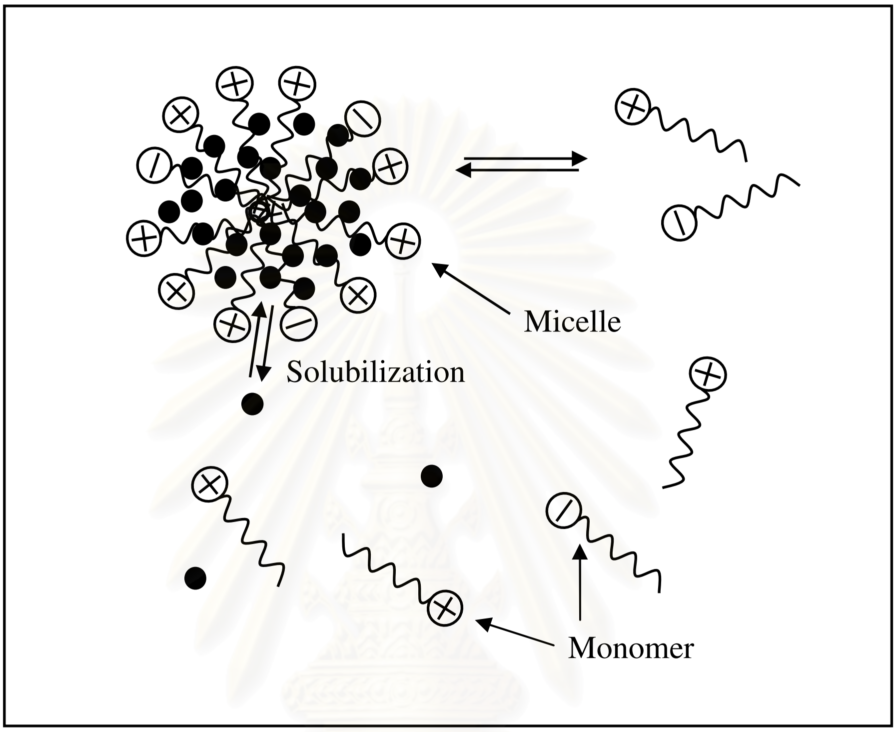


FIG. 2-3. Solubilization of organic solutes in mixed micelles.

2.4 Adsolubilization

When supra-CMC ionic surfactant solutions are contacted with solid surfaces of opposite charge, the surfactant will adsorb on the solid surface and form “adsorbed micelles” or admicelles. Similar to micelles, admicelles have a hydrophobic interior which can solubilize oil, a process known as adsolubilization (O'Haver et al., 1995; Scamehorn et al., 2004b). Adsolubilization can occur in the hydrophobic inner core of the admicelle or in a region of medium polarity located near the surfactant head groups known as the palisade layer (O'Haver et al., 1995). Previous studies (Esumi et al., 1996; Dickson and O’Haver, 2002) indicated that organic solutes tend to partition into the region of the admicelle that has similar polarity to the solute. Thus, while a nonpolar solute is expected to primarily partition within the core region, a polar solute is expected to preferentially adsolubilize in the palisade layer (Figure 2-4). Since adsolubilization may be used to remove organic pollutants from contaminated groundwater or wastewater, it is important to understand the partition of contaminants in the different regions of the admicelle (Esumi et al., 1996; Abe et al., 2000; Esumi et al., 2000; Esumi et al., 2001; Pradubmook et al., 2003; Okamoto et al., 2004).

For adsolubilization studies of styrene and ethylcyclohexane in mixed admicelles (SDS/PODD on silica and SHDPDS/DPCl on alumina), the mole fraction of the organic solute in the admicelle, X_{ads}, can be calculated by Equation 2-6 (Nayyar et al., 1994).

$$X_{adm} = \frac{(S_i - S_f)}{(S_i - S_f) + (A_i - A_f) + (C_i - C_f)} \qquad [2\text{-}6]$$

where X_{adm} is mole fraction of organic solute in admicelle, S_i and S_f are the initial and equilibrium aqueous concentrations of the organic solute, A_i and A_f are the initial and equilibrium aqueous concentrations of anionic surfactant, and C_i and C_f are the initial and equilibrium aqueous concentrations of cationic surfactant.

The admicellar partition coefficient, K_{adm}, is defined similar to the micellar partition coefficient as shown in Equation 2-7 (Rosen, 1989c; Nayyar et al., 1994).

$$K_{adm} = \frac{X_{adm}}{X_{aq}} \qquad [2\text{-}7]$$

For economic reasons, it is important to find ways to improve the solubilization and adsolubilization capacity of surfactant systems. Recent work on microemulsions has found that mixtures of anionic and cationic surfactant help increase the solubilization capacity of these systems (Doan et al., 2003). This finding agrees with previous observations that suggest that mixed anionic and cationic systems (Bergström, 2001) and mixed ionic and nonionic systems (Rosen and Gu 1987; Kunieda et al., 1998; Zhu and Feng, 2003) exhibit synergistic behavior, (i.e. lower CMC, higher solubilization enhancement) when mixed at an appropriate ratio.

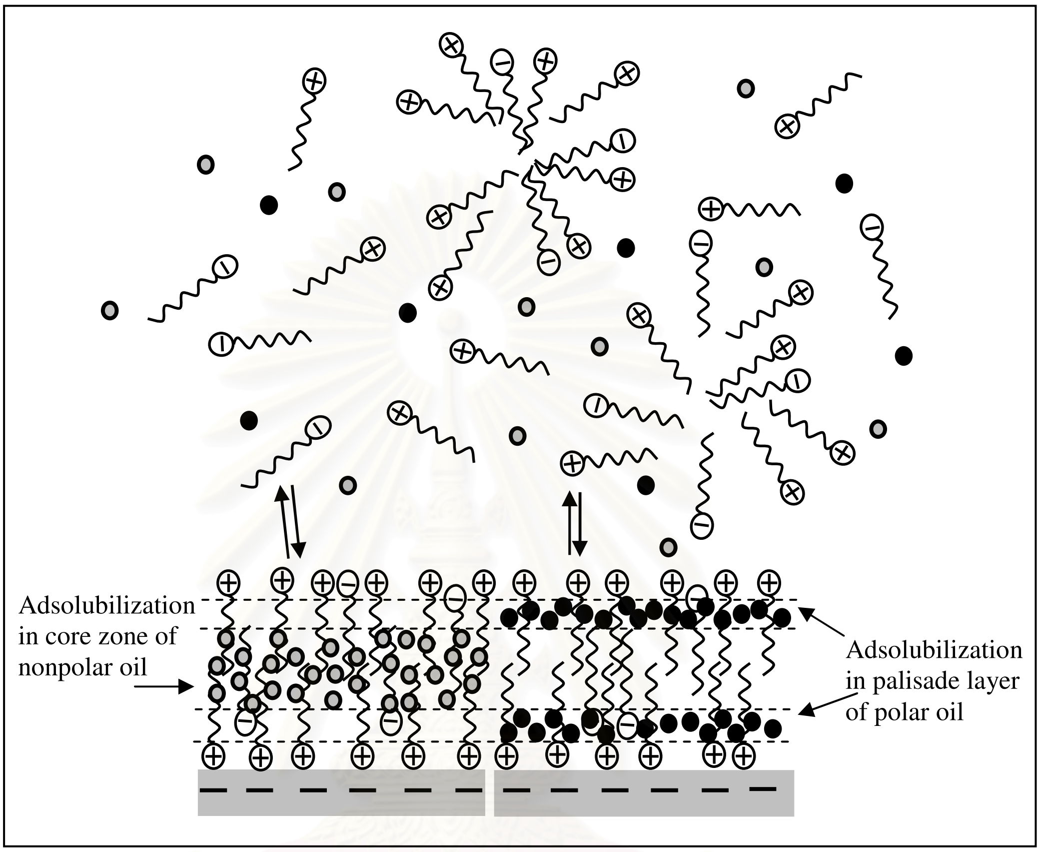


FIG. 2-4. Adsolubilization of organic solutes in core zone of admicelle.

2.5 Column study

Groundwater contamination is a very challenging form of environmental pollution (Fetter, 1988). A common source of groundwater contamination is the accidental release of hydrocarbon fuels and solvents into the subsurface. The widespread detection of organic solvents and other petroleum-based products in groundwater has prompted intensive studies of nonaqueous-phase liquid (NAPL) transport and distribution in subsurface environments (LaGrega et al., 2001). Nonaqueous-phase liquids normally enter the unsaturated zone as discrete liquid phases and are transported downward by gravitational and capillary forces (Lyman et al., 1992). As NAPLs are transported through the subsurface, a portion of the organic phase will be trapped within the soil pores as immobile globules (residual saturation) due to interfacial forces. The low water solubility of most NAPLs causes the residual organic phase to serve as a long-term source of groundwater contamination (Freeze and Cherry, 1979).

Surfactant enhanced groundwater remediation has proven to be much more effective than the conventional pump-and-treat method (Fortin et al., 1997; Li and Rosen, 2000; Sabatini et al., 2000; Mulligan et al., 2001a). Surfactants can be used to increase the solubility of the NAPL constituents in water, or can lower the interfacial tension at the water-NAPL interface and thus mobilize the NAPL (Fountain et al., 1991; Willson et al., 1999).

At concentrations above the critical micelle concentration (CMC), surfactant monomers associate with one another to form micelles which have a hydrophobic interior (Rosen, 1989c). The partition of organic solutes into micelles is called solubilization (Broze, 1995; Scamehorn et al, 2004b). The economics of surfactant-enhanced subsurface remediation is sometimes affected by losses of surfactants due to many phenomena such as precipitation, sorption, liquid crystal, etc. (Doan et al., 2003). To avoid such phenomena, mixed surfactant systems have been studied to minimize surfactant losses (Stellner et al., 1988; Bergström, 2001; Kang et al., 2001; Chen et al., 2002).

The adsorption of surfactant onto the surface of soils forms adsorbed surfactant structures with properties similar to micelles which are thus referred to as admicelles (Esumi et al., 2001). The partition of organic solutes into admicelles is called adsolubilization (Dickson and O'Haver, 2002). The admicelles can be used to create additional sorption sites and thus cause an increased retardation of organic contaminants (Wagner et al., 1994) by acting as a permeable sorptive wall (see Figure 2-5) (US Environmental Protection Agency, 1995). The study of adsorption of surfactants on soil particle surface is also important for predicting the transport of surfactants for the design of groundwater remediation applications and for the fate and transport of surfactants as environmental contaminants themselves (Kibbey and Hayes, 2000). Thus, solubilization and adsolubilization of organic contaminants dissolved in groundwater can be used in groundwater quality management efforts. (Finkel et al., 1999; Behrends and Herrmann, 2000).

The adsolubilization of styrene and ethylcyclohexane in both PODD-alone system and mixed SDS/PODD system can be calculated by the mass balance (Knox et al., 1993), as shown in Equation (2-8).

Mass of chemical adsorbed = (Mass of chemical entering column – Mass of chemical existing column – Mass of chemical in pore water) / mass of solid particle

$$q = \frac{C_0 \cdot V - \int C_d \cdot V - C_0 \cdot V_{pw}}{W_g} \qquad [2\text{-}8]$$

where q is the mass of chemical adsorbed in mole/gram, C_0 is the initial chemical concentration in mole/L, C_d is the time dependent concentration exiting the column during breakthrough, V is volume of chemical injected in L, V_{pw} is volume of pore water in L, and W_g is weight of solid particle in gram.

The adsorption of the surfactant adsorbed onto silica surface can be obtained by Equation (2-2).

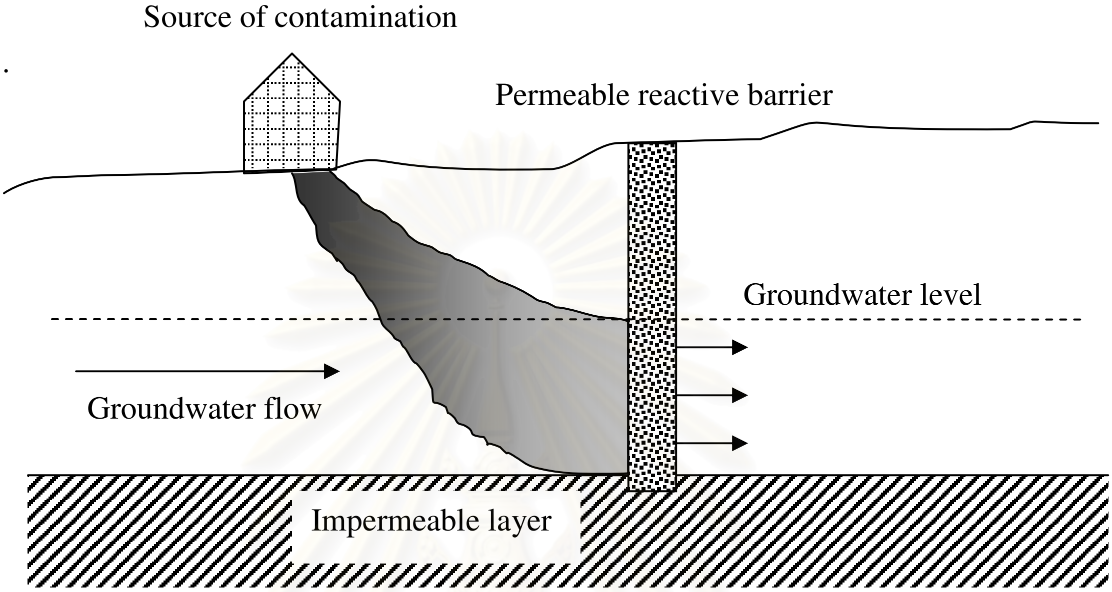


FIG. 2-5 Permeable reactive barrier for groundwater contamination (Adapted from Mulligan et al., 2001b).

2.6 Surface tension study

Since surfactants are highly surface active, one of their main functions is to reduce surface tension (see Figure 2-6). Surface tension studies also can be used for investigating the minimum coverage area (A_{min}) of monolayer surfactant molecule. The A_{min} of the monolayer surfactant molecule can be used as the evidence of the bilayer or double layer of the surfactant molecules which formed admicelles on solid particle surface. The A_{min} of the admicelles which performs bilayer is expected to be at least two times smaller than the A_{min} of the monolayer of the surfactant molecules. While the A_{min} of the admicelle is determined by the adsorption experiments of the surfactants onto solid particle surface, the A_{min} of the monolayer of surfactant was determined by the surface tension experiments with the calculation from Equation 2-9 and Equation 2-10 (Rosen and Gu, 1987; Rosen et al., 1994; Rosen and Song, 1996; Lin et al., 1999; Cui and Canselier, 2000; Medrzycka and Lamparska, 2000; Prosser and Franses, 2001).

$$\Gamma = -\frac{1x10^{-3}}{2.303nRT}\left(\frac{\partial \gamma}{\partial \log C}\right)_T \qquad [2\text{-}9]$$

$$A_{\min} = \frac{1x10^{20}}{N\Gamma} \qquad [2\text{-}10]$$

where Γ is the saturation adsorption values in mole/m^2, γ is the surface tension in mN/m (millinewton per meter), log C is the log surfactant concentration in molar, R is the constant value of 8.31 in joules/mole/K, T is the absolute temperature, K (30 degree celcius, 303.15 K), n is the number of species at the interface whose concentration at the interface (unitless, changes with C $= 1 + \frac{C_{surf}}{C_{surf} + IS} \cong 1$ when the surfactant concentration used to calculate A_{min} are less than 1/10 of the ionic strength

(IS of NaCl = 0.01 M), and N is the Avogadro's number, 6.023×10^{23}. A_{min} is the minimum coverage area in A^o/molecule (divided by 100 to convert to nm^2/molecule).

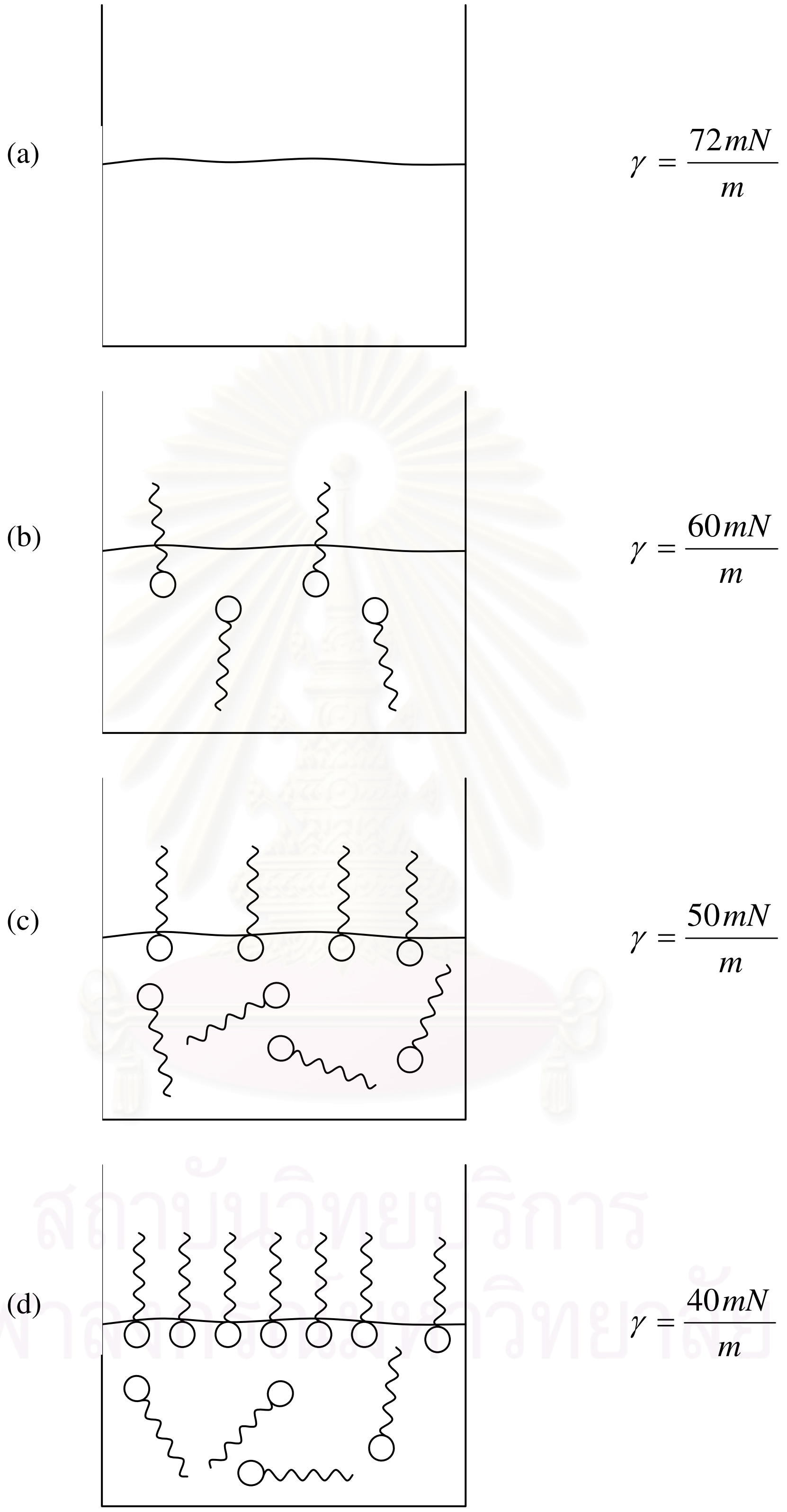


FIG. 2-6 Schematic for surface tension study (Adapted from Sabatini et al., 2003).

2.7 Electron microscope studies

To study the structures, such as surface features, size, shape, and arrangement, of the adsorbent, which has surfactant admicelles adsorbed on the surface, SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) techniques were use. In this research, these methods are used to characterize adsorbents of silica with the admicelle of mixed SDS/PODD, 1:3 ratio (the best ratio of adsorption, solubilization, and adsolubilization from adsorption, solubilization, and adsolubilization experiments, see Chapter IV) and PODD-alone. The formation of ultrathin films polystyrene from styrene adsolubilized in mixed SDS/PODD and PODD-alone admicelles on silica was prepared in order to preserve the structure of admicelles while running the electron microscope. The formation of ultrathin films in adsorbed surfactant, bilayer or admicelles, has been previously investigated both in anionic surfactant on alumina by Wu et al. (1987) and cationic surfactant on silica by O'Haver (1995). The size of silica with and without admicelle adsorbed on the surface is expected to be studied by SEM and TEM in order to confirm the arrangement of bilayer of the surfactants.

2.7.1 SEM (Scanning electron microscopy)

Electron microscopy takes advantage of the wave nature of rapidly moving electrons. Where visible light has wavelengths from 4,000 to 7,000 Angstroms, electrons accelerated to 10,000 KeV have a wavelength of 0.12 Angstroms. Optical microscopes have their resolution limited by the diffraction of light to about 1000 diameters magnification. Electron microscopes, so far, are limited to magnifications of around 1,000,000 diameters, primarily because of spherical and chromatic aberrations. Scanning electron microscope resolutions are currently limited to around 25 Angstroms, though, for a variety of reasons.

The scanning electron microscope generates a beam of electrons in a vacuum. The beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils. The primary imaging method is by collecting secondary electrons that are released by the sample. The secondary electrons are detected by a scintillation material that produces flashes of light from the electrons. The light flashes are then detected and amplified by a photomultiplier tube.

By correlating the sample scan position with the resulting signal, an image can be formed that is strikingly similar to what would be seen through an optical microscope. The illumination and shadowing show a quite natural looking surface topography. The explanation of typical SEMs workings is as shown in Figure 2-7.

The Virtual Source at the top represents the electron gun, producing a stream of monochromatic electrons. The stream is condensed by the first condenser lens. This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam. The beam is then constricted by the condenser aperture, eliminating some high-angle electrons. The second condenser lens forms the electrons into a thin, tight, coherent beam. A user selectable objective aperture further eliminates high-angle electrons from the beam. A set of coils then scan or sweep the beam in a grid fashion, dwelling on points for a period of time determined by the scan speed. The final lens, the Objective, focuses the scanning beam onto the desired region of the specimen. When the beam strikes the sample interactions occur inside the sample and are detected with various instruments. Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number. This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.

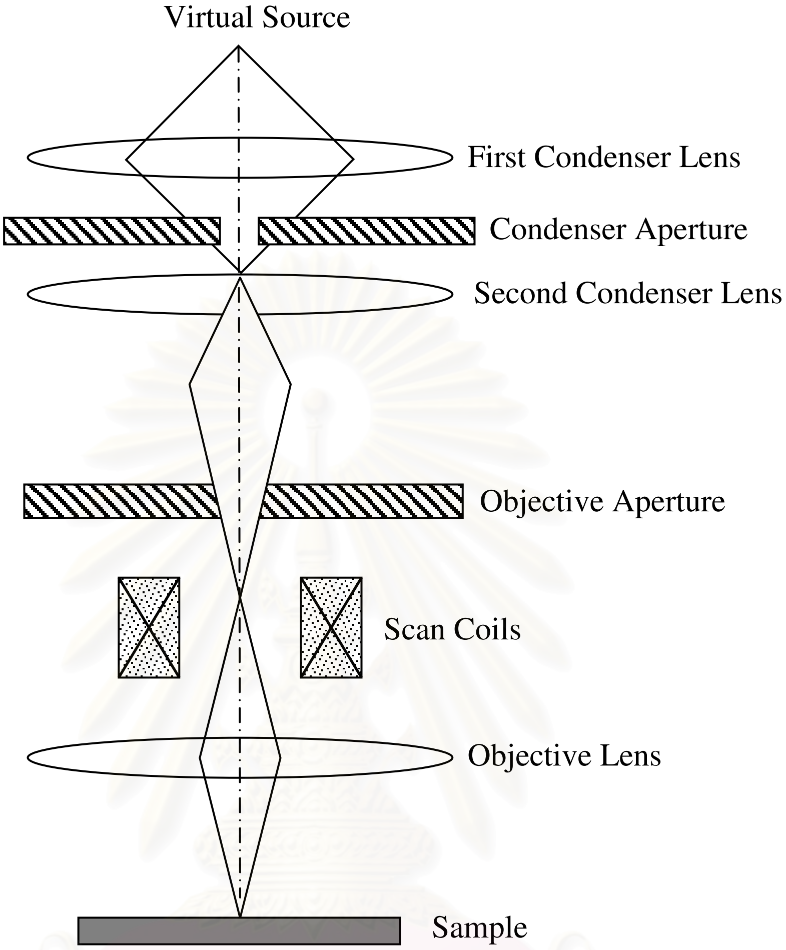


FIG. 2-7 A detailed explanation of how a typical SEM functions. (Modified from http://www.unl.edu/CMRAcfem/semoptic.htm).

2.7.2 TEM (Transmission electron microscopy)

A TEM works much like a slide projector. A projector shines a beam of light through (transmits) the slide, as the light passes through it is affected by the structures and objects on the slide. These effects result in only certain parts of the light beam being transmitted through certain parts of the slide. This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide.

TEMs work in the same way as SEMS except that they shine a beam of electrons through the specimen. Whatever part is transmitted is projected onto a phosphor screen for the user to see. A technical explanation of typical TEMs workings is as shown in Figure 2-8.

The Virtual Source at the top represents the electron gun, producing a stream of monochromatic electrons. This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens largely determines the spot size; the general size range of the final spot that strikes the sample. The second lens actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam. The beam is restricted by the condenser aperture, knocking out high angle electrons. The beam strikes the specimen and parts of it are transmitted. This transmitted portion is focused by the objective lens into an image optional objective and selected area metal apertures can restrict the beam; the objective aperture enhancing contrast by blocking out high-angle diffracted electrons, the selected area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample. The image is passed down the column through the intermediate and projector lenses, being enlarged all the way. The image strikes the phosphor image screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons were transmitted through. The lighter areas of the image represent those areas of the sample that more electrons were transmitted through.

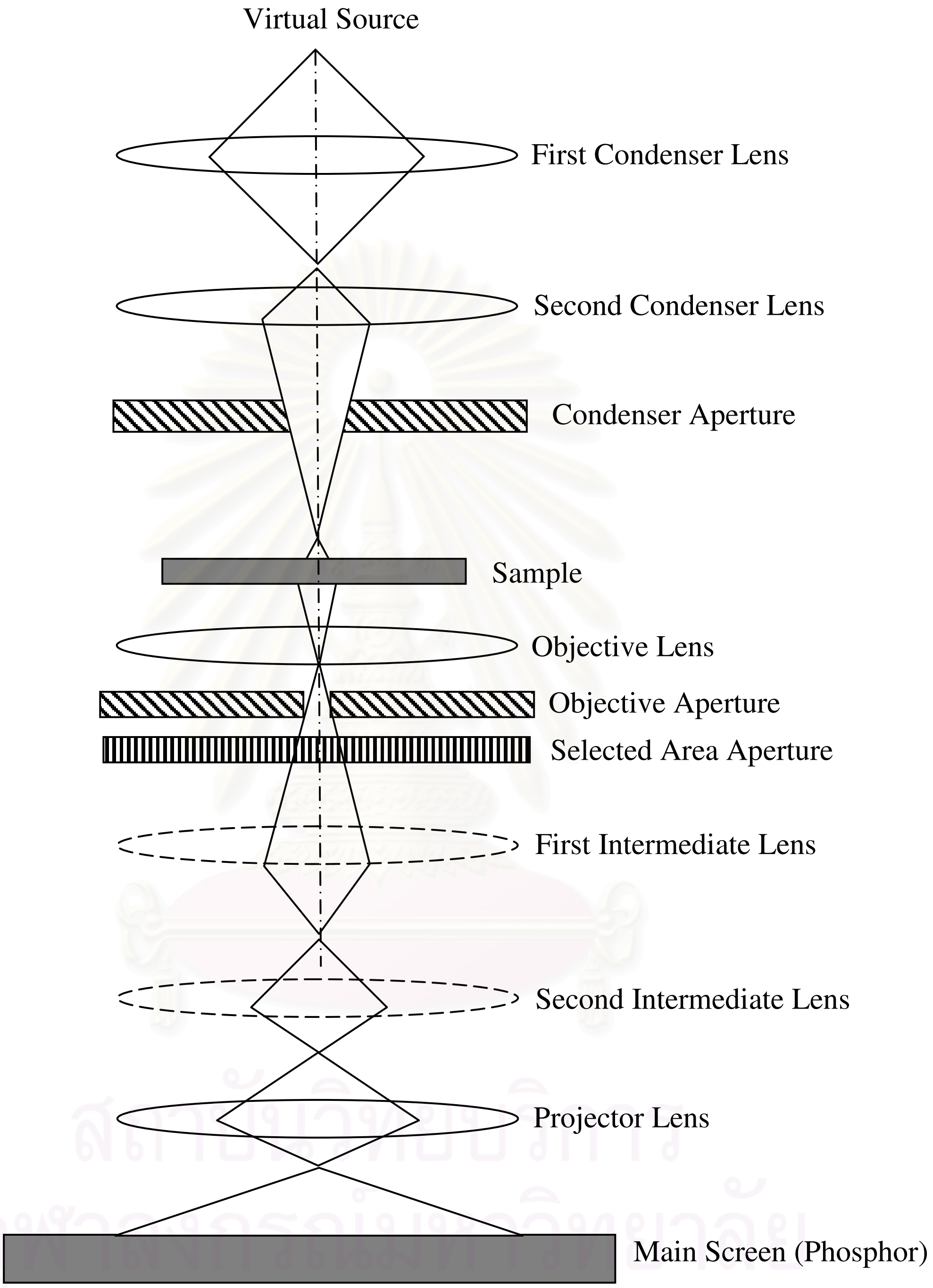


FIG. 2-8 A detailed explanation of how a typical TEM functions. (Modified from http://www.unl.edu/CMRAcfem/temoptic.htm)

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Anionic surfactants

3.1.1.1 The gemini anionic surfactant sodium hexadecyl-diphenyloxide disulfonate (SHDPDS or Dowfax 8390), which is a mixture of mono-hexadecyl and di-hexadecyl diphenyloxide disulfonate (80% and 20%, respectively (Rouse et al., 1993)), was obtained from Dow Chemical Company (Midland, MI) (36% active).

3.1.1.2 The single anionic surfactant sodium dodecyl sulfate (SDS, 98% active) was purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received.

3.1.2 Cationic surfactants

3.1.2.1 The twin-head cationic surfactant pentamethyl-octadecyl-1,3-propane diammonium dichloride (PODD or Duoquad ® T50) was donated by Akzo Nobel Surface Chemistry LLC (McCook, IL) as a 50 % solution in isopropanol; while mainly octadecyl (38% C18-1 and 25% C18), PODD is also 29% hexadecyl with the remaining 8% being C14, C14-1, C16-1, and C18-2. The isopropanol was evaporated by cyclic heating at 80°C under vacuum extraction. The purified sample was re-diluted and titrated until the remaining alcohol was < 1 %.

3.1.2.2 The single cationic surfactant dodecylpyridinium chloride (DPCI, 98% active) was purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received.

3.1.3 Organic solutes

3.1.3.1 Polar organic solute styrene (99%) was purchased from Fisher Chemicals (Fairlawn, NJ).

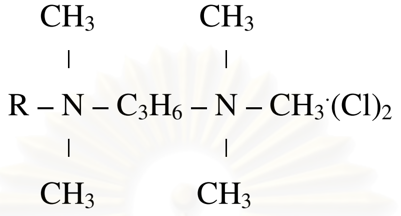
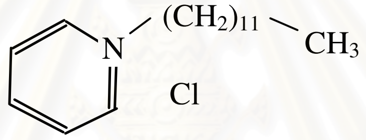
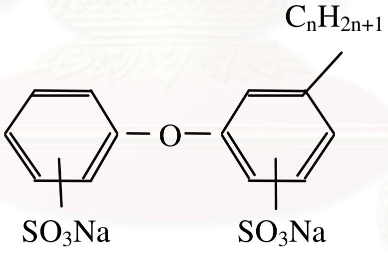
3.1.3.2 Non-polar organic solute ethylcyclohexane (98%) was purchased from Aldrich Company (Milwaukee, WI).

The chemical properties of the surfactants and solutes are shown in Table 3-1 and Table 3-2, respectively.

3.1.4 Initiator

The initiator for polystyrene, [2-(Acryloyloxy) ethyl](4-benzoyl benzyl) dimethyl ammonium bromide or DMAB were purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received. The chemical properties of the initiator is shown in Table 3-3.

TABLE 3-1 Chemical properties of surfactants.

Chemicals	Molecular structure	Molecular weight, g/mole	CMC, mM
Pentamethyl-octadecyl-1,3-propane diammonium dichloride[a,b] (PODD)	 $R-\underset{CH_3}{\overset{CH_3}{N}}-C_3H_6-\underset{CH_3}{\overset{CH_3}{N}}-CH_3\cdot(Cl)_2$	463.62	1.3[c] (0.01 M NaCl)
Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}SO_4\ Na$	288.38	6.8[d] (0.15 M NaCl)
Dodecylpyridinium chloride (DPCl)		283.88	4.0[d] (0.15 M NaCl)
Sodium hexadecyl-diphenyloxide disulfonate (SHDPDS)		642	6.3e (0.15 M NaCl)

[a] http://surface.akzonobelusa.com/cfm/2page2.cfm?PID=100

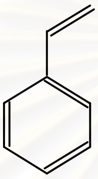
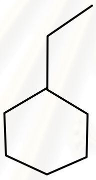
[b] http://www.lion.co.jp/laco/e/prod/p/44dqad_e.htm

[c] Fuangswasdi et al., 2005a.

[d] Stellner, et al., 1988.

[e] Rouse, et al., 1993.

TABLE 3-2 Chemical properties of oils.

Chemical	Molecular structure	Molecular Weight (g/mole)	Water solubility (mole/L)	Log K_{ow}	Density g/cm^3	Vapor Pressure (mm Hg)
Styrene[a, b]	C_8H_8 	104.15	0.0027	2.95	0.9045	5 (highly volatile)
Ethylcyclohexane[c, d]	C_8H_{16} 	112.24	0.00056	3.13	0.788	N/A

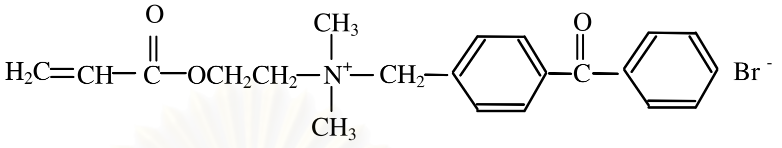
[a] http://www.epa.gov/OGWDW/dwh/t-voc/styrene.html

[b] http://chemfinder.cambridgesoft.com/result.asp

[c] http://chemfinder.cambridgesoft.com/result.asp

[d] http://risk.lsd.ornl.gov/tox/profiles/ethylbenzene.doc

TABLE 3-3 Chemical properties of the initiator.

Chemical	Molecular Structure	Molecular Weight, g/mole
[2-(Acryloyloxy) ethyl](4-benzoyl benzyl)dimethyl ammonium bromide[a] (DMAB)		418.32

[a] data from http://www.thermo.com/eThermo/CMA/PDFs/Product/productFile_1000001344628.pdf

3.1.5 Mineral oxides

3.1.5.1 Alumina oxide (Al_2O_3), mesh size 150, was purchased from Aldrich Chemical Company and has a reported point of zero charge of 9.1 and a measured specific surface area of 133 m^2/g.

3.1.5.2 Silica Hi-sil ® 233 (SiO_2) was donated by PPG Industries Inc., with a reported point of zero charge of 2 to 4 and a measured specific surface area of 143 m^2/g.

The BET specific surface area of the mineral oxides was determined using a Micromeritics model Flow Sord II 2300 instrument. The samples were prepared by heating while simultaneously evacuating or flowing gas (nitrogen as the adsorbed gas and helium as the carrier gas) over the sample to remove the liberated impurities. The prepared samples were then cooled with liquid nitrogen and analyzed by measuring the volume of gas adsorbed at specific pressures (Rouquerol et al., 1994).

Anionic and cationic surfactant concentrations were measured using a Dionex ion chromatograph in reversed-phase mode using an IonPac NS1 column (Dionex, Sunnyvale, CA) with a water-acetonitrite mixture as a mobile phase containing either 10 mM of tetrabutyl ammonium hydroxide or 10 mM of methane sulfuric acid as coupling agents for anionic and cationic surfactants, respectively. The individual coupling agent forms a neutral complex with one of the surfactants, which is then chromatographically separated in the NS1 column. The effluent from the column is contacted with an anionic suppressor (ASRS, 4 mm; Dionex) or cationic suppressor (CSRS, 4 mm; Dionex), causing the complex to decouple and thus allow the surfactant to be detected by conductivity using a CD-25 conductivity detector. All calibration runs resulted in a linear fit with good correlations ($R^2 > 0.99$).

Styrene and ethylcyclohexane concentrations were measured by gas chromatography using a Varian 3300 GC equipped with a 50 m SPB25 hydrophobic capillary column, an auto sampler model 8100 and flame ionization detector (FID). Additional details on this method can be found elsewhere (Acosta et al., 2004).

The surface tension study was measured by the tensiometer model, Kruss digital tensiometer K10T. The polystyrene adsorbent samples were analyzed by SEM model JEOL JSM-880 high resolution scanning electron microscope, and by TEM model JEOL 2000-FX intermediate voltage (200,000 volt).

The experiments for SDS/PODD and SHDPDS/DPCl systems were carried out using 0.01 M and 0.015 M NaCl, respectively, to maintain a constant ionic strength. The experiments were conducted at 25^{o}C ± 1^{o}C with at least duplicate samples; for selected experiments triplicates were run and error bars are included with these data (typical variations for batch experiments were ± 8 % and for column experiments were ± 4 %).

3.2 Methods

3.2.1 Precipitation studies of SDS and PODD.

To study their precipitation, surfactant systems were prepared in 20 mL vials with Teflon-lined caps with either 0.01 M or 0.15 M NaCl (the latter for comparison to data from previous research). The solutions were supercooled at 0° C for 2 days to prevent supersaturation effects. The samples were then placed in a water bath shaker at constant temperature ($30.0 \pm 0.1\ ^{o}C$) for 4 days. The precipitation phase boundaries were determined by visual inspection according to the procedure described by Stellner et al., 1988.

3.2.2 Adsorption experiments.

The adsorption of SDS and PODD was evaluated individually and in mixtures (initial ratios 1:3 and 1:10, cationic-rich) and at various initial concentrations in 40 mL vials. The vials were shaken for 2 days to reach equilibrium at $25^{o}C \pm 1^{o}C$. The pH of the solution was checked and adjusted in the range of 6 to 7 using NaOH and HCl solutions; if pH adjustment was required, the vials were shaken again for one day. Five mL of the supernatant sample was taken from each vial after centrifuging at 2,000 to 2,500 rpm for 30 minutes. The samples were subsequently measured by HPLC for both anionic and cationic surfactants. The surfactant adsorption was calculated according to Equation 2-2 in Chapter II. A similar procedure was used for SHDPDS and DPCl, individually and for SHDPDS/DPCl mixtures at ratios of 3:1, 10:1, 30:1, anionic-rich.

3.2.3 Solubilization study.

The methodology of solubilization and adsolubilization relies on the results of precipitation and adsorption experiments, which are mentioned in Chapter IV. The appropriate ratio of the mixed surfactants and the CMC of the mixed surfactants from Chapter IV are used to design the solubilization and adsolubilization experiments.

The solubilization capacities of styrene and ethylcyclohexane were measured for SDS and PODD alone and for differing concentrations of SDS/PODD mixtures in 1:3 and 1:10 ratio; these ratios were selected to be outside the precipitation region (see Figure 4-1). (eight to nine concentrations for each ratio). A 10-mL aliquot of each surfactant solutions was pipetted into 15 mL vials, followed by addition of an excess amount of solute oil (500 μL styrene or 400 μL ethylcyclohexane) which were subsequently sealed with Teflon caps. The solutions were slowly shaken for 1 day to let the oils solubilize in the aqueous solutions. After centrifuging for 30 minutes, the aqueous surfactant solutions were carefully sampled (1.5 mL for each sample). The concentration of styrene and ethylcyclohexane was measured using gas chromatography (GC). The solubility studies of mixed SHDPDS/DPCl in the ratios 3:1, 10:1, SHDPDS alone, and DPCl alone were conducted in the same manner. The ratios for SHDPDS/DPCl were selected to be outside the precipitation region as (see Figure 4-2).

3.2.4 Adsolubilization study.

Supra-CMC surfactant solutions (20 mL samples in 40 mL vials) of PODD alone and SDS/PODD mixtures were contacted with a given mass of silica in such a way that the final total aqueous surfactant concentration (after adsorption) was just below the CMC (i.e. just below maximum adsorption) for the particular surfactant sample to make sure that no micelles remained in solution after adsorption. Styrene or ethylcyclohexane were added at concentrations less than their solubilization capacity. The volume of oil adsolubilized was calculated by the difference in concentration between the initial and final aqueous concentration of the oil (Nayyar et al., 1994). Blank samples (without silica) were used to assess potential volatilization of the solutes, which was shown to be negligible. The samples were shaken for 2 days which is sufficient to achieve equilibrium as established from unpublished studies and from previous work (Kitiyanan et al., 1996; Wang et al., 1999). The solution pH was maintained in the range of 6 to 7 by using NaOH and HCl solutions if pH adjustment was required; in that case, the vials were shaken again for one day. The samples were centrifuged and a sample of the aqueous solution was collected to measure surfactant and solute concentrations. The same approach was used for mixed SHDPDS/DPCl and SHDPDS-alone adsorbed onto alumina.

3.2.5 Column experiments

Column experiments were designed based on results of adsorption experiments. The CMC of mixed SDS/PODD from the adsorption experiments gives the limit of the surfactant concentrations in column experiments. The column study of SHDPDS and DPCl is not conducted in this research due to the results of the CMCs of SHDPDS-alone and mixed SHDPDS/DPCl showed the same pattern. Thus, it is assumed that the results from the column experiments of SHDPDS-alone and mixed SHDPDS/DPCl will be in the same trend.

The column studies were conducted using Chromaflex borosilicate glass chromatography columns which were 2.5 cm in diameter and 15 cm in length. A total of 2 grams of silica Hi-Sil 233 and approximately 30 grams of glass beads are packed incrementally and homogeneously until the height was 5 cm in the column. The glass beads were added to reduce the effective reactive (adsorptive) length of the column. The column media was saturated by introducing deionized water, which was degassed using helium; flow was from the bottom in the column. Silicone tubing was utilized in the pump and Teflon tubing elsewhere in an effort to eliminate adsorptive losses. A peristaltic high precision pump (Masterflex® L/S digital standard drive, Cole-Parmes Instrument) was used to maintain a constant flow rate (0.36 mL/min). Nitrate (in the form of 0.01 M $NaNO_3$) was used as a conservative tracer during column studies with silica. Sodium nitrate breakthrough was monitored by using an UV/VIS spectrophotometer (DVW-10, D-Star Instruments) at the wave length of 240 nm. The schematic for surfactant & oil / water flushing experiment is shown in Figure 3-1.

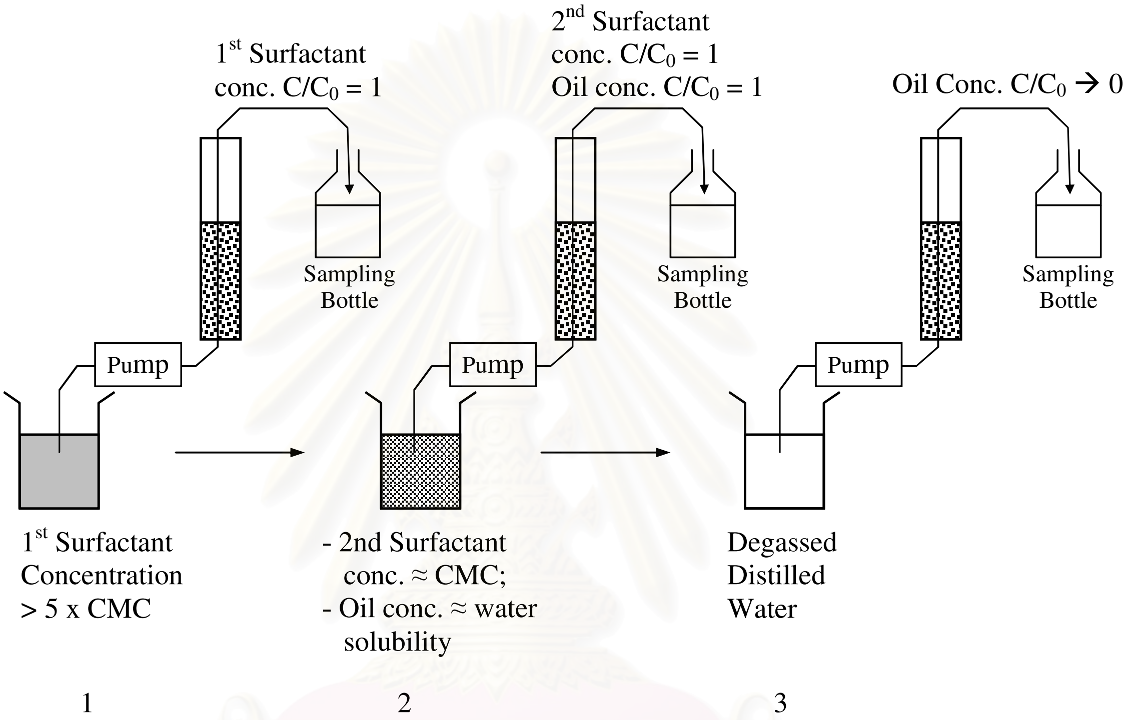


FIG. 3-1 Setup for surfactant & oil / water flushing experiment.

Styrene and ethylcyclohexane were studied at concentrations below their water solubility, which are 2.7 mmole/L and 0.12 mmole/L, respectively. After the tracer study, styrene and ethylcyclohexane were pumped in an upward mode at constant flow (0.36 mL/min). Distilled water was subsequently pumped through the bottom of the column to evaluate desorption of solute and surfactant from the column. The concentrations of styrene and ethylcyclohexane were analyzed by UV/VIS spectrophotometer.

Surfactant was adsorbed on the silica-packed columns by using PODD-alone and by using the optimum ratio of mixed SDS/PODD, 1:3 (cationic-rich) flowing through the column. The surfactant concentrations entering the column were above the critical micelle concentration (CMC), which were 0.02 M and 0.004 M for PODD-alone and mixed SDS/PODD, respectively, to expedite establishment of the surfactant bilayer in the column.

For adsolubilization studies, the adsorption isotherms of PODD-alone and mixed SDS/PODD were used to determine an appropriate concentration of the surfactants upon introduction of styrene and ethylcyclohexane. The appropriate concentration from adsorption isotherm was just below the CMC of the surfactant (transition point) to ensure the maximum surfactant coverage without the presence of micelles in the bulk solution (see Figure 4-5). Thus, the concentrations of PODD-alone and mixed SDS/PODD were 0.001 M and 0.0004 M, respectively.

Adsolubilization experiments of styrene through silica adsorbent, with PODD-alone admicelle adsorbed on the surface, packed in the column was conducted. The mixed solution of styrene, 2.7 mM, and PODD-alone, 1.0 mM, was pumped through the column in an upward mode with constant flow rate. The concentration of styrene was analyzed by UV spectrophotometer. A similar procedure was used for styrene and mixed SDS/PODD system using 2.7 mM styrene, and 0.4 mM SDS/PODD with a 1:3 ratio.

Adsolubilization experiments of ethylcyclohexane through the silica adsorbent with PODD-alone and with mixed SDS/PODD, 1:3 ratio, were conducted using the same procedure as with styrene. The concentration of ethylcyclohexane was 0.56 mM, while the concentrations of surfactants were the same as styrene's procedure. The concentrations of ethylcyclohexane were analyzed by UV spectrophotometer.

The adsolubilization of styrene and ethylcyclohexane in both PODD-alone system and mixed SDS/PODD system were calculated by Equation 2-8 in Chapter II. The amount of surfactant adsorbed onto silica surface was obtained by Equation 2-2 in Chapter II.

Breakthrough curves were plotted as relative styrene or ethylcyclohexane concentration (C/C_0) versus relative pore volume (volume eluted / pore volume). Then the retardation factors can be determined and compared between systems. This step is to compare the retardations of styrene and ethylcyclohexane while passing through silica adsorbent with PODD-alone admicelle and with mixed SDS/PODD admicelle in the column.

3.2.6 Admicelle stability in batch experiments

Supra-CMC surfactant solutions (20 mL samples in 40 mL vials) of PODD alone and SDS/PODD mixtures were contacted with a given mass of silica in such a way that the final total aqueous surfactant concentration (after adsorption) was just below the CMC (i.e. just below maximum adsorption) for the particular surfactant sample to make sure that no micelles remained in solution after adsorption. The samples were shaken for 2 days to achieve equilibrium (Fuangswasdi et al., 2005a). The samples were centrifuged at 2,000 to 2,500 rpm for 30 minutes and the supernatant was measured by HPLC for both anionic and cationic surfactants to check the concentrations of SDS and PODD. Thus, we can calculate the concentrations of the admicelles adsorbed on silica surface before the adsorbent was rinsed by distilled water. Then, the samples were rinsed by distilled water, shaken for one hour, centrifuged for 30 minutes, and the supernatant was subsequently measured by HPLC for both anionic and cationic surfactants. Rinsing was repeated five times. The concentrations of surfactants desorbed from the adsorbent during each washing were plotted on the graph to compare the stability of the PODD-alone admicelles and the mixed SDS/PODD, 1:3 ratio, admicelles.

3.2.7 Surface Tension Experiments

The surface tension of SDS and PODD were measured individually and in mixing ratio 1:3 (cationic-rich) at various concentrations. The measurements were conducted at 30°C with 0.01 M NaCl in order to have the same concentration of electrolyte as the previous study of adsorption. The surface tension measurements were made by the Wilhelmy vertical plate technique, using a sand-blasted platinum blade of ca. 5-cm perimeter suspended from the arm of a Bethlehem dial-type torsion balance.

3.2.8 Electron Microscope Studies

3.2.7.1 Polystyrene - Ultrathin Film Formation

The method used for the modification of mineral surface particles by the formation of ultrathin films was conducted. The formation of admicelles followed by adsolubilization of monomers into the admicelle and then polymerization of the monomers in-situ constitutes a three step process (Figure 3-2) to construct a thin layer on a solid substrate via a low energy process (Wu et al., 1987; O'Haver, 1995).

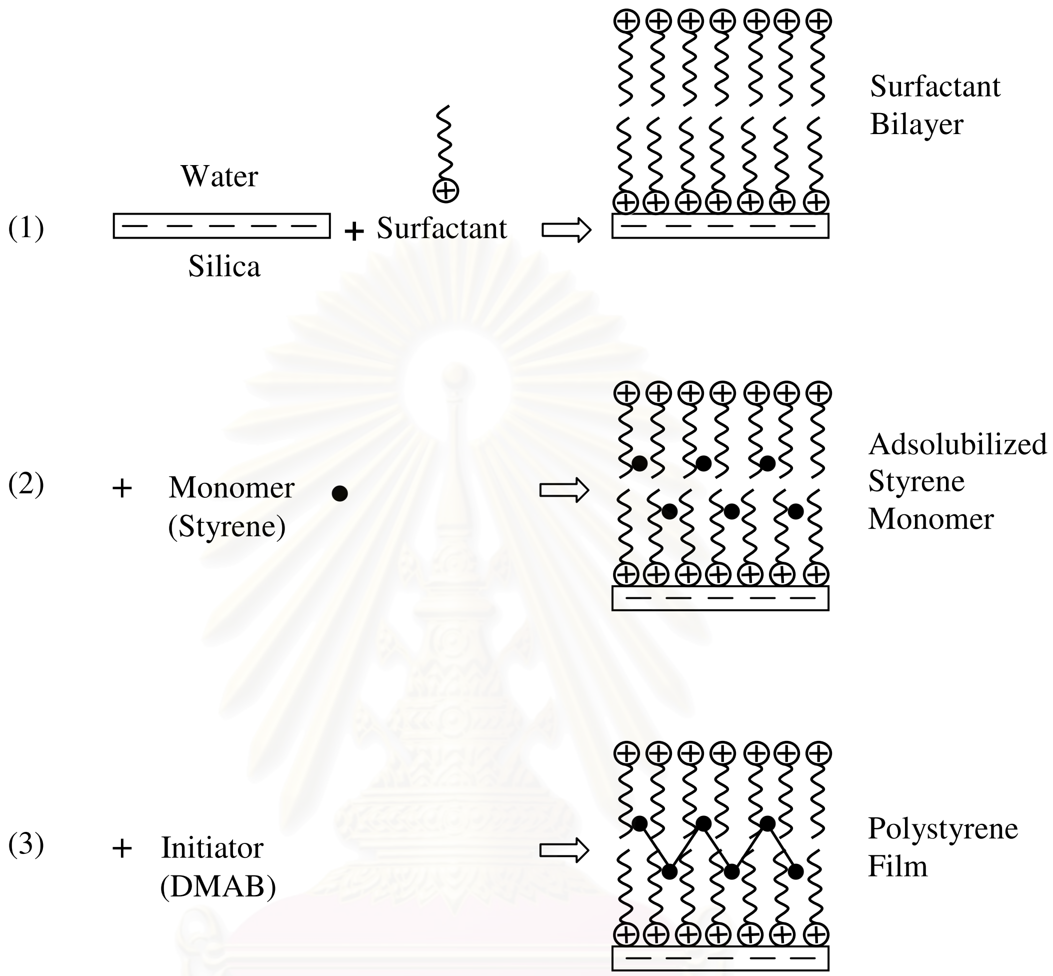


FIG. 3-2 Schematic of the proposed film-forming process: (1) surfactant adsorption on substrate (silica) and formation of the admicelle; (2) concentration of monomer within the bilayer; (3) initiation of polymerization.

From Figure 3-2, step (1) consists of admicelle formation by the adsorption of a surfactant bilayer onto the surface of the substrate. Adsorption is accomplished through the use of a suitable surfactant under appropriate system conditions. The choice of surfactant is influenced by the point of zero charge of the substrate, the chemical nature of the polymer to be formed, and the chosen polymerization initiator system. A study of the point of zero charge (PZC) for the substrate provides information on the pH ranges in which cationic or anionic surfactants may readily be utilized. The instability or dissolution of components in certain pH ranges may further define the range of useful operating conditions, and hence, surfactant type.

Step (2) in the process is the solubility of monomer into the admicelle, a phenomenon called adsolubilization. Many organic monomers are nearly insoluble in water. Thus, at equilibrium, they preferentially partition into the hydrophobic interior of the admicelle. This process can occur after the formation of the admicelles, or concurrently with surfactant adsorption. It is convenient experimentally to dissolve the monomer, and sometimes the initiator ([2-(Acryloyloxy)ethyl](4-benzoylbenzyl) dimethylammonium bromide), in the surfactant feed solution prior to surfactant adsorption. In these cases, the presence of micelles promotes the solubility of the monomer in the feed solution, increases the rate of the adsolubilization of the monomer in the admicelles, and helps prevent the formation of emulsions. When this feed solution is contacted with the mineral substrate, the adsorption of the micelles is thought to carry the solubilized monomer onto the substrate surface.

Step (3) is the in-situ polymerization of the monomer. For free radical polymerization, this is accomplished by the generation of radicals capable of initiating the polymerization reaction. In some cases, the compatibility of the initiator system with anionic or cationic surfactants may also affect the choice of an appropriate surfactant a suitable reaction conditions. To reduce the chance of polymerization in the bulk solution, a detailed study of adsorption and adsolubilization isotherms are made to insure that the system equilibrates with the surfactant concentration in the bulk solution below the critical micelle concentration (CMC). Once the reaction has started, additional monomer from the bulk solution diffuses into the admicelle (Rosen and Gu, 1987). If the reaction is continued for a sufficient length of time, virtually all monomer can be converted to polymer.

3.2.7.2 SEM (Scanning Electron Microscopy)

The polymerized adsorbents, which consist of mixed SDS/PODD admicelle, 1:3 ratio, PODD-alone admicelle, and the silica without admicelle, were scanned for studying the surface features by using SEM (Scanning Electron Microscopy), JEOL JSM-880 high resolution scanning electron microscope.

3.2.7.2 TEM (Transmission Electron Microscopy)

The polymerized adsorbents, both with admicelle SDS/PODD, 1:3 ratio and PODD-alone, and the silica without admicelle adsorbed on the surface were studied for the size, shape and arrangement of the particles by using TEM (Transmission Electron Microscopy), model JEOL 2000-FX intermediate voltage (200,000 volt).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Precipitation studies

While adsorption studies were the focus of this research, precipitation studies were conducted to make sure that our adsorption studies were in regions where precipitation did not occur. Nonetheless, while not comprehensive, the precipitation studies provide some valuable insights that are worthy of discussion. Figure 4-1 shows the precipitation phase diagrams for the SDS/PODD system at added NaCl concentration of 0.01 M and 0.15 M and for 25^{o}C vs. 30^{o}C, respectively. At 0.15 M NaCl and 30^{o}C, the SDS/PODD system did not exhibit precipitation, but showed only a very small region of liquid crystal formation; this region did not exist at 25^{o}C. This is in contrast to the precipitation region observed for SDS/PODD at the lower salt concentration of 0.01 M and 25^{o}C, and the much larger precipitation regime for SDS/DPCl at 0.15 M NaCl and 30^{o}C. In the SDS/DPCl system, both anionic and cationic surfactants have linear hydrophobic groups of the same length (12 carbons) and we will refer to this system as symmetric-linear. The PODD is both branched in the hydrophobe and has two cationic head groups, so the SDS/PODD system is both asymmetric and nonlinear. In previous work as shown in Figure 4-2, we used a branched monovalent anionic surfactant (SDHS) or a branched divalent anionic surfactant (SHDPDS) with a linear cationic surfactant (DPCl). Below the CMC, the SHDPDS/DPCl system has even less tendency to precipitate than the SDS/DPCl system, and the SDHS/DPCl system even less tendency to precipitate (compare

Figure 4-1 and Figure 4-2). Precipitation phase boundaries for SDS/DPCl have been compared to those with smaller alkyl chains in the anionic surfactant (n = 8 and 10 compared to 12) (Amante et al., 1991) and the tendency to precipitate below the CMC is less as n decreases. It is not clear how much of this effect is due to the mismatch (asymmetry) between the alkyl chain lengths of the anionic and the cationic surfactant (Shiao et al., 1998) and how much is due to the smaller hydrophobe. The significant reduction of precipitation for the SDS/PODD system in Figure 4-1 shows that below the CMC, we can greatly reduce the precipitation with a model anionic surfactant although we cannot yet identify the exact mechanism (e.g. alkyl chain branching, asymmetry due to the dissimilar surfactant alkyl chain lengths, valency effects by using a multiply-charged, asymmetric branched cationic surfactant).

Above the CMC, the tendency to precipitate is a consequence of two competing forces: the solubility product and the tendency to form micelles. This can lead to contrasting trends to those below the CMC. For example, above the CMC, the SDHS/DPCl system has a much broader precipitation region than SHDPDS/DPCl (Figure 4-2) indicating that the branching of the anionic surfactant can reduce the tendency to form micelles more than the effect on the K_{sp}. For systems with varied alkyl chain lengths for alkyl sulfate/DPCl, the precipitation phase boundaries above the CMC are not greatly altered. For both the SHDPDS/DPCl system in Figure 4-2 and the SDS/PODD system in Figure 4-1, the precipitation region above the CMC is considerably less than for SDS/DPCl system. Therefore, while the nuances of the effect of surfactant structure on precipitation are not totally clear, it appears that having either the anionic or the cationic surfactant with multiple charges tends to greatly shrink the precipitation phase boundary above the CMC.

It should be noted that in Figure 4-1, we include data from Stellner et al. (1988) for SDS/DPCl which was conducted at 0.15 M NaCl while our work with SDS/PODD was conducted at 0.01 M NaCl. The additional NaCl for the SDS/DPCl system will tend to lower the CMC for this system and thus shrink the precipitation regime; nonetheless, the SDS/DPCl system still demonstrates a much larger precipitation diagram. The smaller size of the precipitation region allows the formulation of systems with ratios that more closely approach equimolar concentrations, where the maximum synergism is typically observed for anionic and cationic mixtures. As an example, for 1 mM PODD, as much as 3 mM SDS can be added without precipitation, but for the SDHS/DPCl system at 1 mM of DPCL, the addition of 3 mM of SDS results in precipitation (see Figure 4-1).

Based on the precipitation data in Figure 4-1, adsorption experiments of SDS/PODD were evaluated at initial ratios of 1:3 and 1:10, while SHDPDS/DPCl adsorption was studied at initial ratios of 3:1, 10:1, and 30:1, respectively, in order to avoid precipitation. While the precipitation work is at 30^{o}C and the adsorption data is at 25^{o}C, the adsorption studies are done far enough from the precipitation boundaries that this difference is not significant.

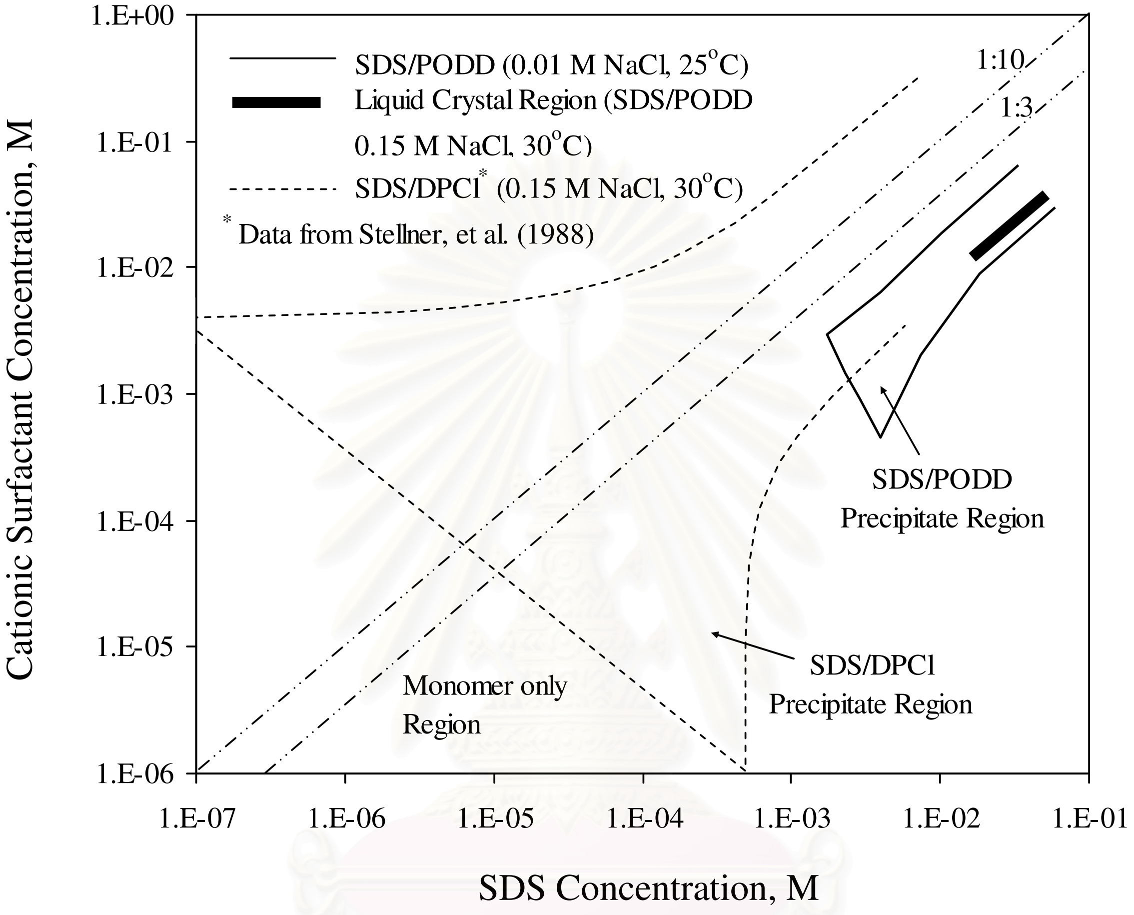


FIG. 4-1 Precipitation diagram of asymmetric ionic head group mixed surfactant SDS/ PODD at 0.01 M NaCl. (Data for the SDS/DPCl precipitation diagram from Stellner et al. (1988), 0.15 M NaCl is shown for comparison). The lines labeled 1:10 and 1:3 correspond to a constant 1:10 and 1:3 molar ratios of SDS/cationic surfactant, respectively, for varying surfactant concentrations.

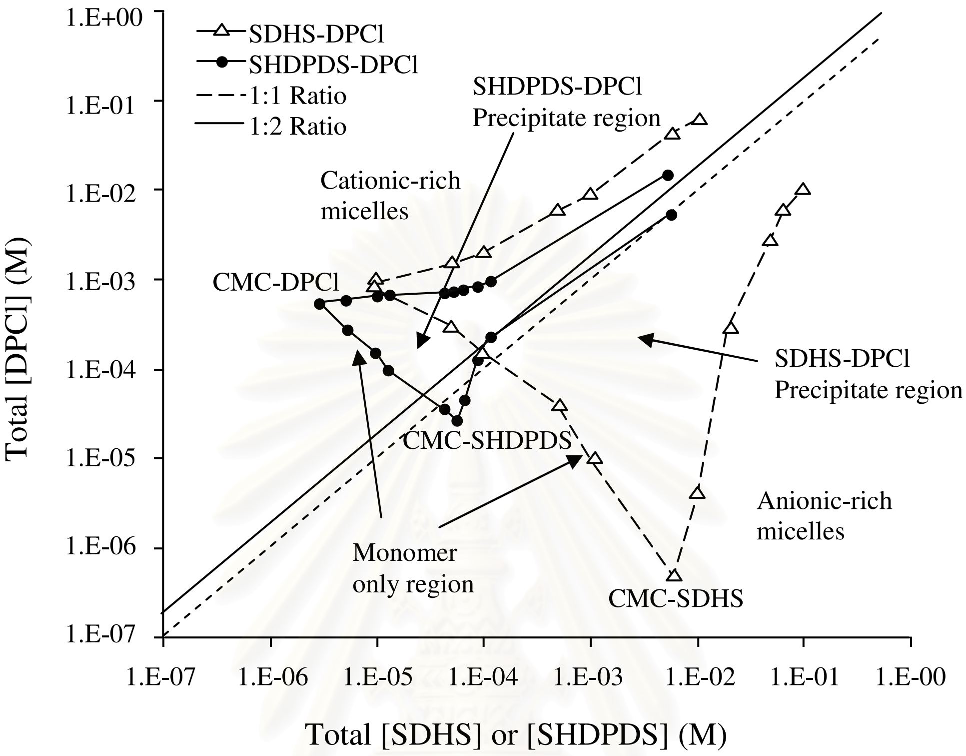


FIG. 4-2 Precipitation diagrams for mixed surfactant systems, sodium dihexyl sulfosuccinate and dodecylpyridinium chloride (SDHS/DPCl), and diphenyloxide disulfonate and dodecylpyridinium chloride (SHDPDS/DPCl), 0.15 M NaCl, 25°C. (Adapted from Doan et al. (2003)).

4.2 Adsorption experiments

The adsorption isotherms for PODD and SDS individually and SDS/PODD mixtures on silica are shown in Figure 4-3, Figure 4-4, and Figure 4-5, respectively (in 0.01 M NaCl at 25°C). Adsorption experiments of SDS/PODD were evaluated at initial ratios of 1:3 and 1:10, while SHDPDS/DPCl adsorption was studied at initial ratios of 3:1, 10:1, and 30:1 (in 0.015 M NaCl at 25°C); these ratios were selected to avoid precipitation. Analytical detection limits prevented measurement of surfactant concentrations in Region I and the Regions II to III transition is not readily distinguishable (see Figure 4-3). Selected points were measured in triplicate to assess the magnitude of the experimental precision; the resulting error bars proved to be similar in magnitude to the size of the data symbols (± 4 to 7 %). For PODD concentrations greater than 1×10^{-4} M, the adsorption of PODD is virtually the same when using PODD alone or at an initial ratio of 1:10 SDS/PODD; thus, adding a small concentration of SDS did not significantly affect the adsorption of PODD. However, when using an initial SDS/PODD ratio of 1:3 a measurable increase in the total adsorption was observed over the PODD alone; thus, a minimum amount of the oppositely charged surfactant (SDS) is necessary to reduce the charge repulsion between adjacent surfactant molecules (PODD) and thus increase the adsorption density of the PODD, as demonstrated in previous research (Patist et al., 1999).

Figure 4-4 shows SDS adsorption on silica when SDS coexists with PODD. Data for SDS alone is not shown because SDS adsorption was negligible on silica, as expected since both the SDS and silica are negatively charged at neutral pH (silica has with a reported point of zero charge of 2 to 4). However, the SDS co-adsorbs when present with PODD and shows increased adsorption at higher initial surfactant ratios (SDS/PODD, 1:10 and 1:3).

Figure 4-5 presents the total surfactant adsorption isotherms (PODD plus SDS). While the initial SDS/PODD ratio of 1:10 has only a minor effect on the adsorption isotherm, at the initial ratio of 1:3, a stronger adsorption synergism is observed, as observed by both higher plateau adsorption (4.0 versus 1.8 molecule/nm^2 - see Table 4-1) and in reaching that plateau adsorption at a lower surfactant concentration (0.50 versus 1.4 mM - see Table 4-1). The fact that the plateau adsorption occurs at a lower surfactant concentration is expected from the lower CMC of mixed anionic-cationic surfactant systems.

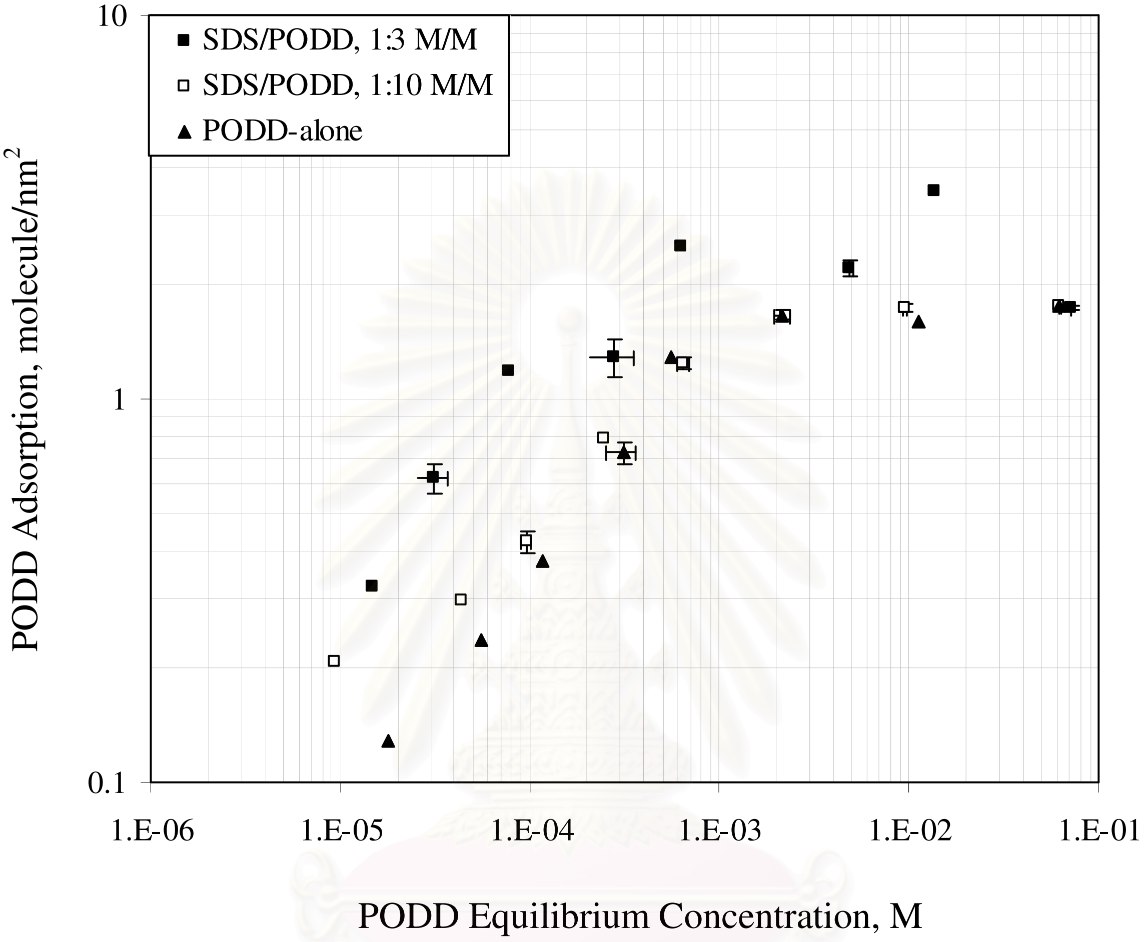


FIG. 4-3 Cationic surfactant, pentamethyl-octadecyl-1,3-propane diammonium dichloride (PODD), adsorption onto silica for PODD-alone and PODD mixed with sodium dodecyl sulfate (SDS). (0.01 M NaCl, 25°C).

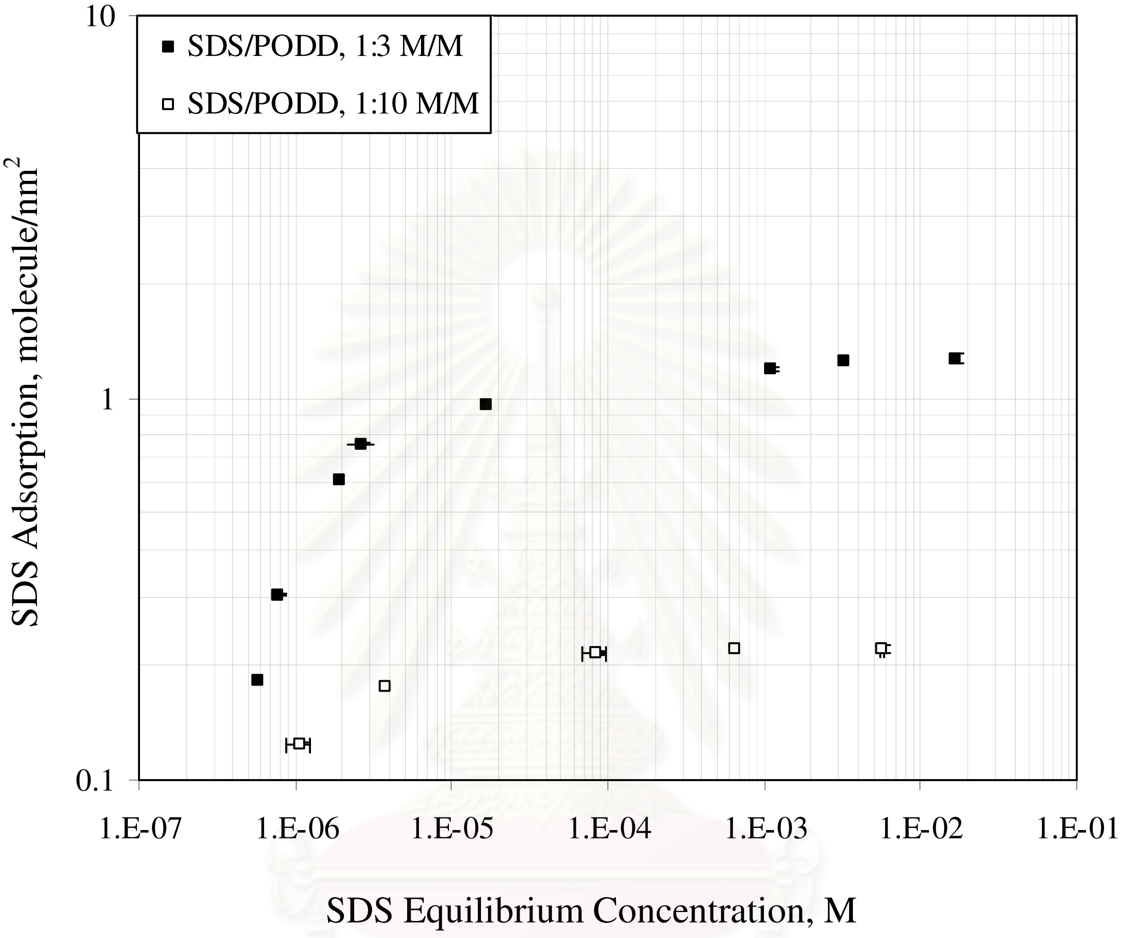


FIG. 4-4 Anionic surfactant (SDS) adsorption onto silica for mixed SDS/PODD system (0.01 M NaCl, 25°C); note: SDS-alone adsorption on silica was negligible.

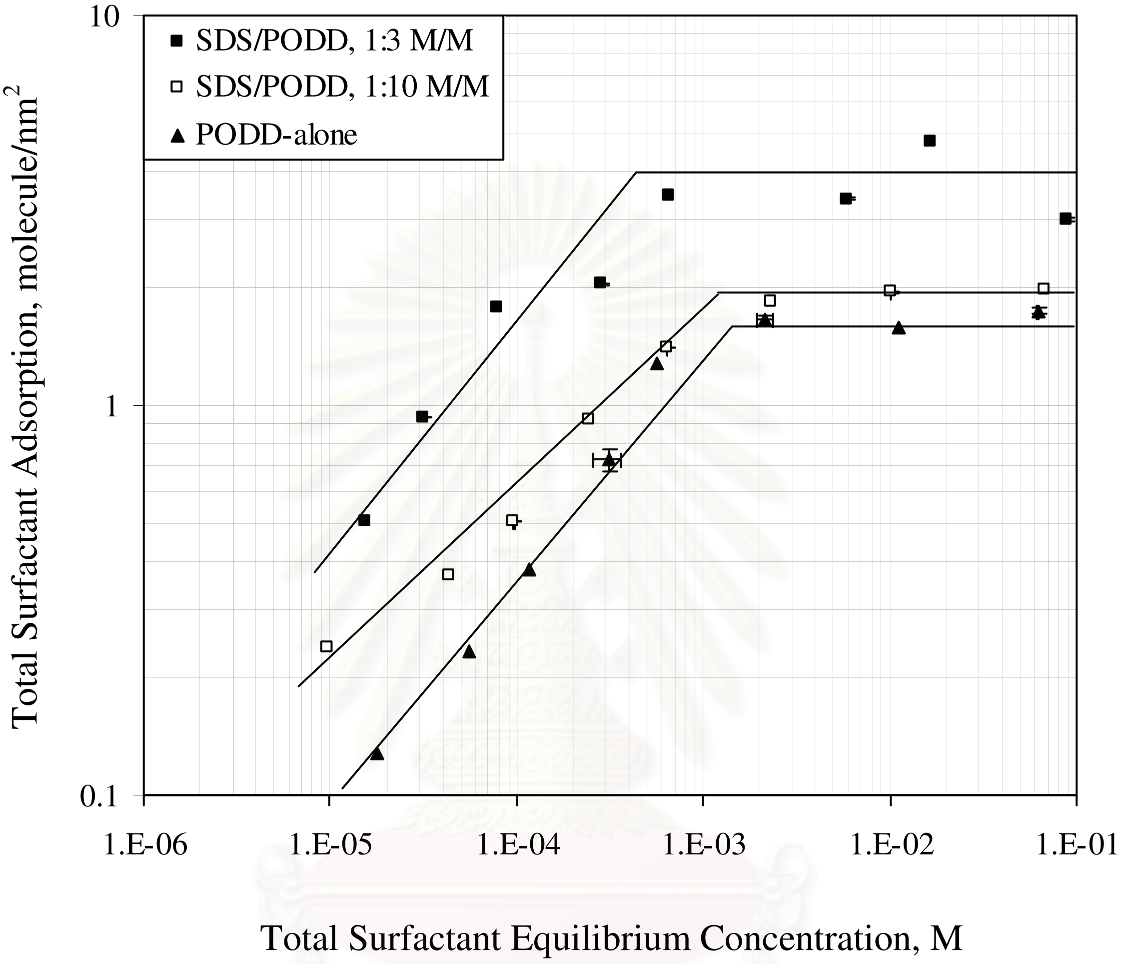


FIG. 4-5 Total surfactant (SDS and PODD) adsorption onto silica for PODD-alone and mixed SDS/PODD system (0.01 M NaCl, 25^{o}C); note: SDS-alone adsorption on silica was negligible.

TABLE 4-1 Adsorption and CMC of mixed and single surfactant systems.

Medium	Structure Initial Concentration Ratio	Plateau Adsorption									Plateau Aqueous Surfactant Concentration mM (CMC)
		Cationic Surfactant			Anionic Surfactant			Total Surfactant			
		molecules/ nm^2	nm^2/ molecule	mole/g	molecules/ nm^2	nm^2/ molecule	mole/g	molecules/ nm^2	nm^2/ molecule	mole/g	
Silica	SDS/PODD, 1:3	2.8	0.36	6.6x10^{-4}	1.2	0.8	2.8x10^{-4}	4.0	0.25	9.5x10^{-4}	0.50
	SDS/PODD, 1:10	1.9	0.53	4.5x10^{-4}	0.20	5.0	4.7x10^{-5}	2.1	0.48	5.0x10^{-4}	1.20
	PODD-alone	1.8	0.56	4.3x10^{-4}	NA[a]	NA	NA	1.8	0.56	4.3x10^{-4}	1.40
Alumina	SHDPDS/DPCl, 3:1	0.36	2.8	7.3x10^{-5}	1.0	1.0	2.0x10^{-4}	1.4	0.74	2.8x10^{-4}	0.55
	SHDPDS/DPCl, 10:1	0.13	7.7	2.6x10^{-5}	1.1	0.88	2.3x10^{-4}	1.3	0.79	2.6x10^{-4}	0.43
	SHDPDS/DPCl, 30:1	0.05	20.0	1.0x10^{-5}	1.1	0.91	2.2x10^{-4}	1.2	0.87	2.3x10^{-4}	0.46
	SHDPDS-alone	NA	NA	NA	1.1	0.92	2.2x10^{-4}	1.1	0.92	2.2x10^{-4}	0.49

[a] NA - Not Applicable - The adsorption of like-charged surfactant alone and media was below detection limits.

Figure 4-6, Figure 4-7, and Figure 4-8 show surfactant adsorption on alumina for SHDPDS, DPCl and combined SHDPDS/DPCl, respectively. Another relevant characteristic of the curves in Figure 4-6 is that the addition of the cationic surfactant DPCl did not significantly affect the adsorption of SHDPDS, even when present at ratios as high as 3:1. The reason for the lack of SHDPDS adsorption synergism is still unclear, but the extreme reduction in the precipitation region for SHDPDS (see below) suggests steric hindrances that may also limit synergism in adsorption. In Figure 4-7, DPCl adsorption results are only shown for the ratio of 3:1 and 10:1 because the ratio of 30:1 showed insignificant adsorption (less than 0.1 molecule/nm^2). It is interesting to note that, even though SHDPDS did not show enhanced adsorption in the presence of the DPCl, the DPCl did co-adsorb with SHDPDS, as SDS did in mixtures with PODD above. Thus, while the surfactant adsorption itself did not show significant synergism, the co-adsorption of DPCl with SHDPDS may still alter the properties of the adsorbed layer, as will be assessed in a companion paper.

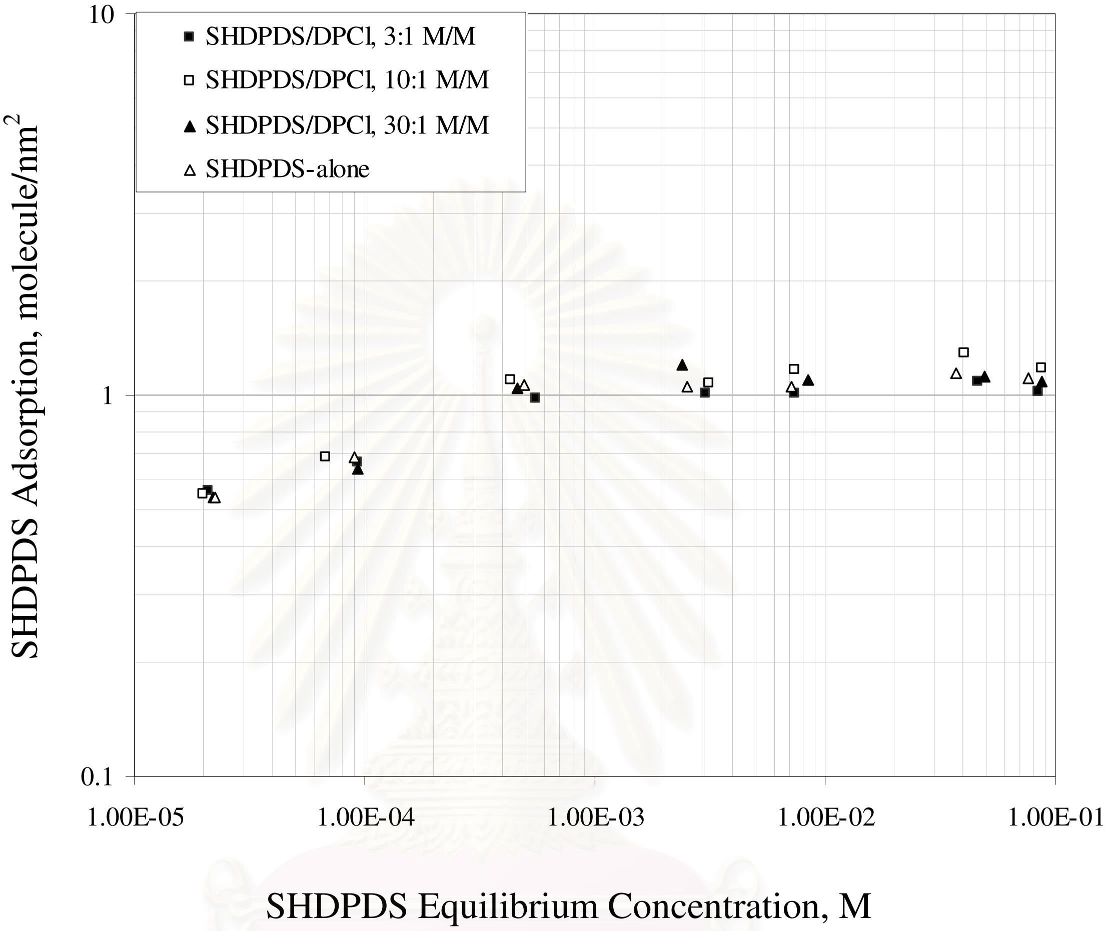


FIG. 4-6 Anionic surfactant (SHDPDS) adsorption onto alumina for mixed SHDPDS/DPCl system (0.015 M NaCl, 25^{o}C).

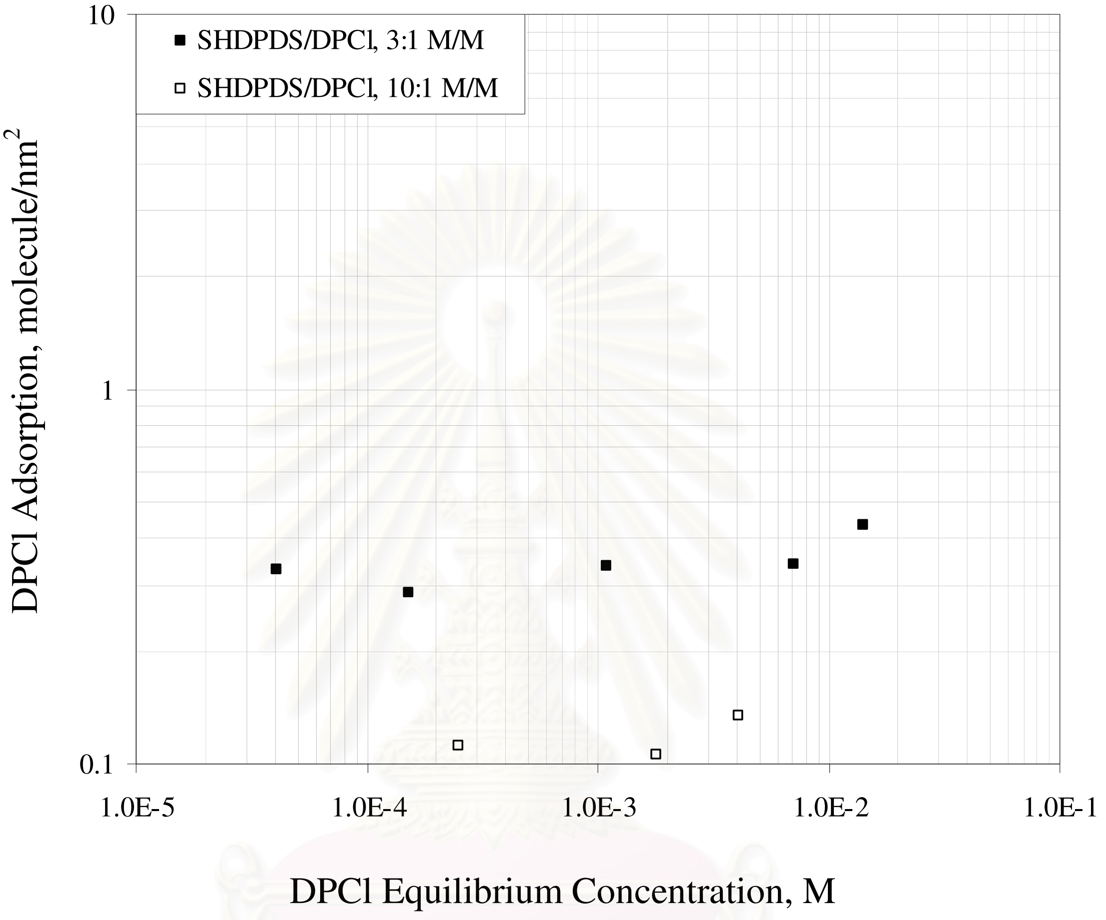


FIG. 4-7 Cationic surfactant (DPCl) adsorption onto alumina for mixed SHDPDS/DPCl system (0.015 M NaCl, 25°C); note: Adsorption results for the initial ratio of 30:1 and for DPCl-alone are not shown because they were negligible.

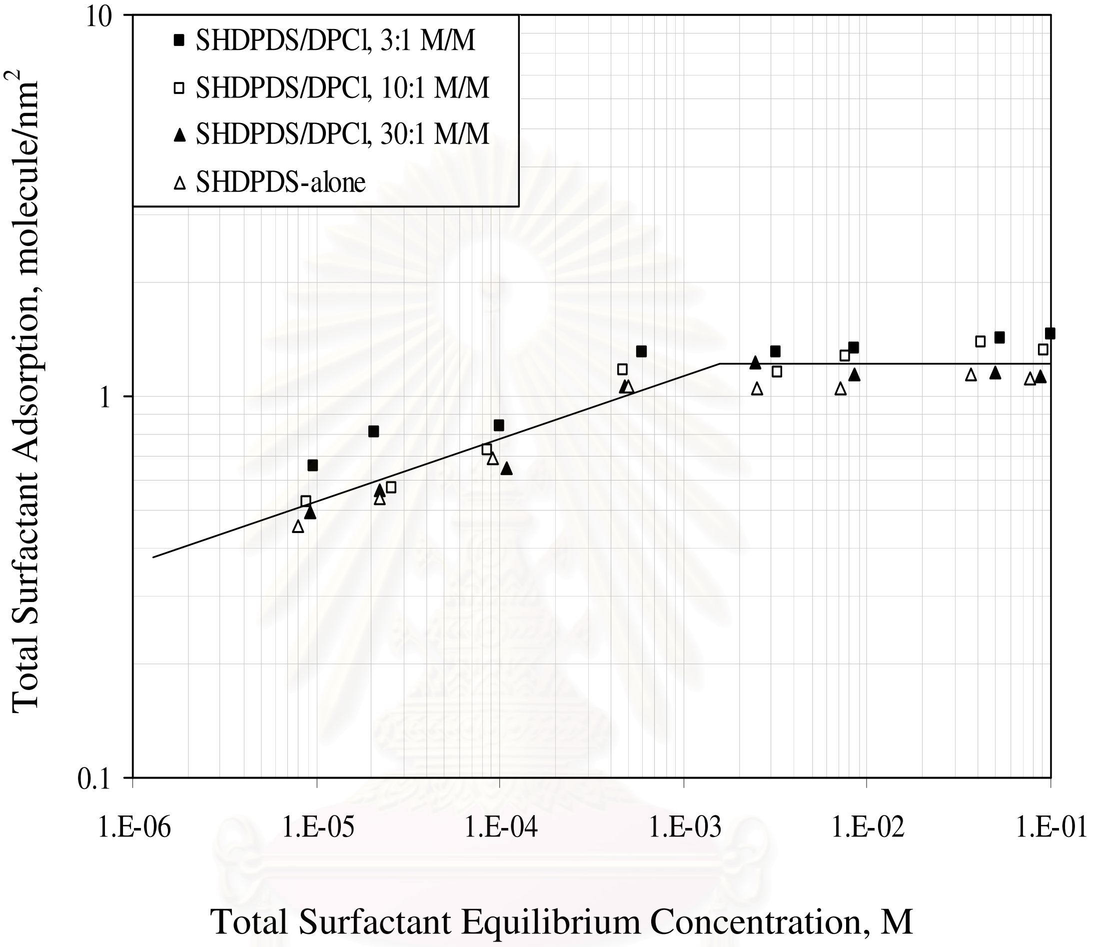


FIG. 4-8 Total surfactant (SHDPDS and DPCl) adsorption onto alumina for SHDPDS-alone and for mixed SHDPDS/DPCl systems (0.015 M NaCl, 25°C).

4.3 Solubilization in micelles

The results of the styrene and ethylcyclohexane solubilization experiments in mixed SDS/PODD, SDS-alone, and PODD-alone micelles are shown in Figure 4-9 and Figure 4-10, respectively. Figure 4-9 plots the solubility of styrene versus surfactant concentration. At low surfactant concentrations (below the CMC), the styrene solubility is constant (the plot is horizontal) and equals the water solubility, while at higher surfactant concentrations (above the CMC), the styrene solubility increases linearly due to solubilization in micelles. The intersection of these two lines identifies the CMC of the system, as noted in the figure. The slope of the plot above the CMC is the MSR, which along with the solubility of the solute can be used to calculate the K_{mic} (see Equations 2-3 to 2-5 in Chapter II). The solubilization of styrene and ethylcyclohexane in mixed SHDPDS/DPCl, SHDPDS-alone, and DPCl-alone micelles are shown in Figure 4-11 and Figure 4-12, respectively.

Figure 4-13 and Figure 4-14 show the molar solubilization ratios (MSRs) of oils in mixed micelles of SDS/PODD and SDS-alone and PHDD-alone and in mixed micelles of SHDPDS/DPCl and SHDPDS-alone and DPCl-alone, respectively.

The CMC, MSR, and K_{mic} values for each of these of these systems are summarized in Table 4-2. The CMC is affected by the presence of the solutes, so the values in Table 4-2 are different than for surfactant-only systems at those salinities.

Mixtures of SDS and PODD produced lower CMC values in comparison to the individual surfactants alone (Figure 4-9 and Figure 4-10, respectively and Table 4-2); this effect is more evident as the ratio of anionic to cationic surfactant approaches equimolar concentrations. The micellar partition coefficient (K_{mic}) values for styrene and ethylcyclohexane are higher for the SDS/PODD mixtures than for either the SDS alone or PODD system alone (see Table 4-2), which supports the original hypothesis that mixed anionic-cationic micelles will show higher solubilization capacity compared to single surfactant micelles. In addition, the K_{mic} of ethylcyclohexane in mixed SDS/PODD and PODD-alone micelles is higher than that of styrene.

The different partition behavior between ethylcyclohexane and styrene can be explained by the fact that the non-polar ethylcyclohexane tends to concentrate in the hydrophobic core of the micelles (Scamehorn et al., 2004a). The higher K_{mic} values for non-polar ethylcyclohexane in mixed SDS/PODD systems suggest that the mixed anionic/cationic surfactant micelles have a larger and more hydrophobic non-polar core region than the individual surfactant micelles. By contrast, the styrene is expected to accumulate in the palisade layer, which would experience less synergism, or even be negatively affected, by the mixed micelles due to the “squeezing out” effect; i.e. the second surfactant fills “cavities” in the micelle where the solute might have accumulated (Scamehorn et al., 2004a). Conversely, it has been shown that the π electron/charged group interactions between cationic head groups and aromatic solutes can produce higher solubilization in cationic micelles (ion-dipole interactions) (Scamehorn and Harwell, 1988). Thus, while is it surprising that ethylcyclohexane (E) solubilizes more than styrene (S) in cationic micelles here, it is interesting to note that the ratio of K_{mic} for E/S is less in SDS and SHDPDS than for DPCl or PODD, consistent with this discussion. These interpretations are speculative at this point and should be further evaluated in future research.

Table 4-2 also summarizes the CMC, MSR and K_{mic} values for mixed SHDPDS/DPCl, SHDPDS-alone and DPCl-alone micelles. The CMC values of the surfactant mixtures were nearly the same as that for the SHDPDS alone. The CMC of the mixtures is virtually the same as for the SHDPDS alone, and the K_{mic} values are unaffected by the mixtures. These results are consistent with previous research with SHDPDS which shows that it is not significantly impacted by counterions or cosurfactants, as demonstrated by precipitation and middle phase microemulsion studies (Doan et al., 2003).

These results raise the question as to the kind of micellar structure a double head, single tail ionic surfactant forms when combined with a single head ionic surfactant of opposite charge. One can imagine that a single head ionic surfactant could complex with the double head, single tail surfactant to form a quasi-double head - double tail structure. A ratio of 1:3 of SDS/PODD could produce a double tail complex that would account for 33% of the total PODD. This more hydrophobic double head - double tail structure would approach the hydrophobicity of the SHDPDS system. In fact the K_{mic} for ethylcyclohexane in SDS/PODD at a ratio 1:3 approaches the value of this parameter for the SHDPDS-alone system.

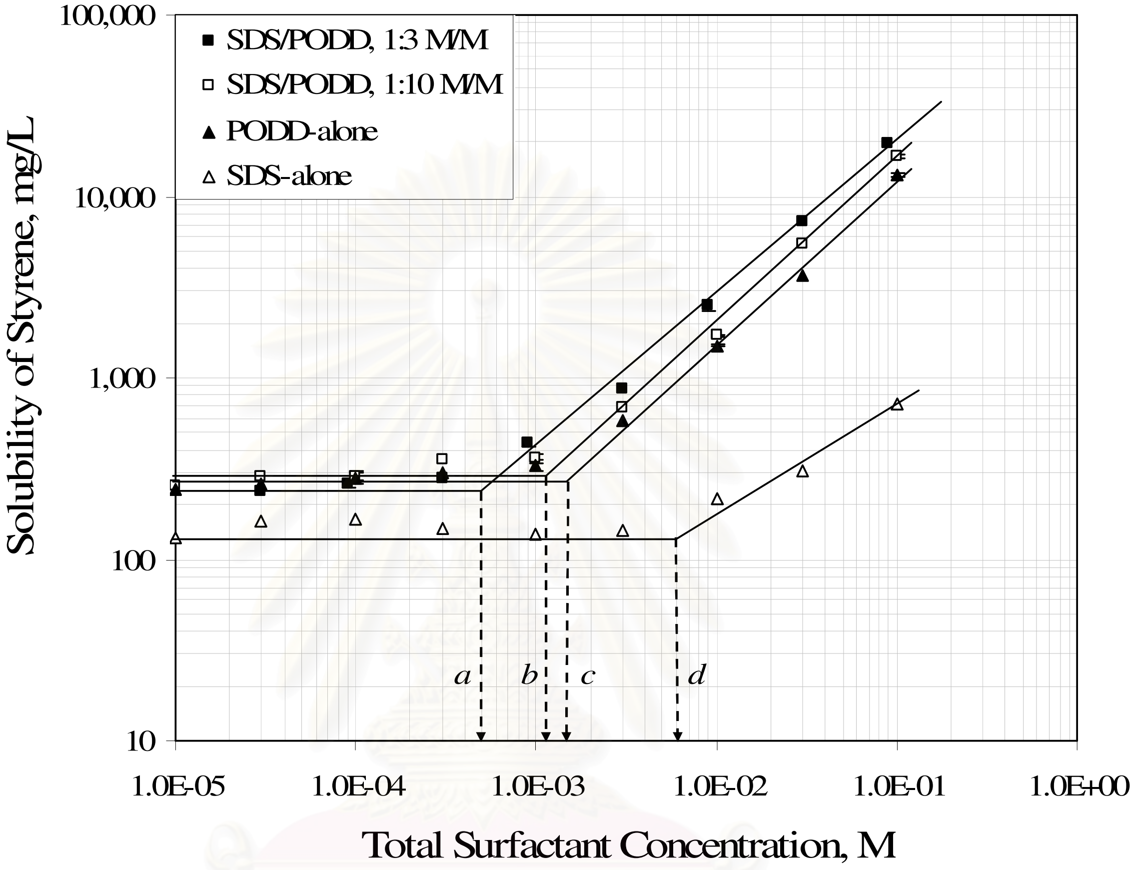


FIG. 4-9 Solubilization of styrene in sodium dodecyl sulfate (SDS-alone), pentamethyl-octadecyl-1,3-propane diammonium dichloride (PODD-alone) and in two SDS/PODD mixtures (0.01 M NaCl, 25^{o}C). (*a* is the CMC of SDS/PODD, 1:3; *b* is the CMC of SDS/PODD, 1:10; *c* is the CMC of PODD-alone; and *d* is the CMC of SDS-alone).

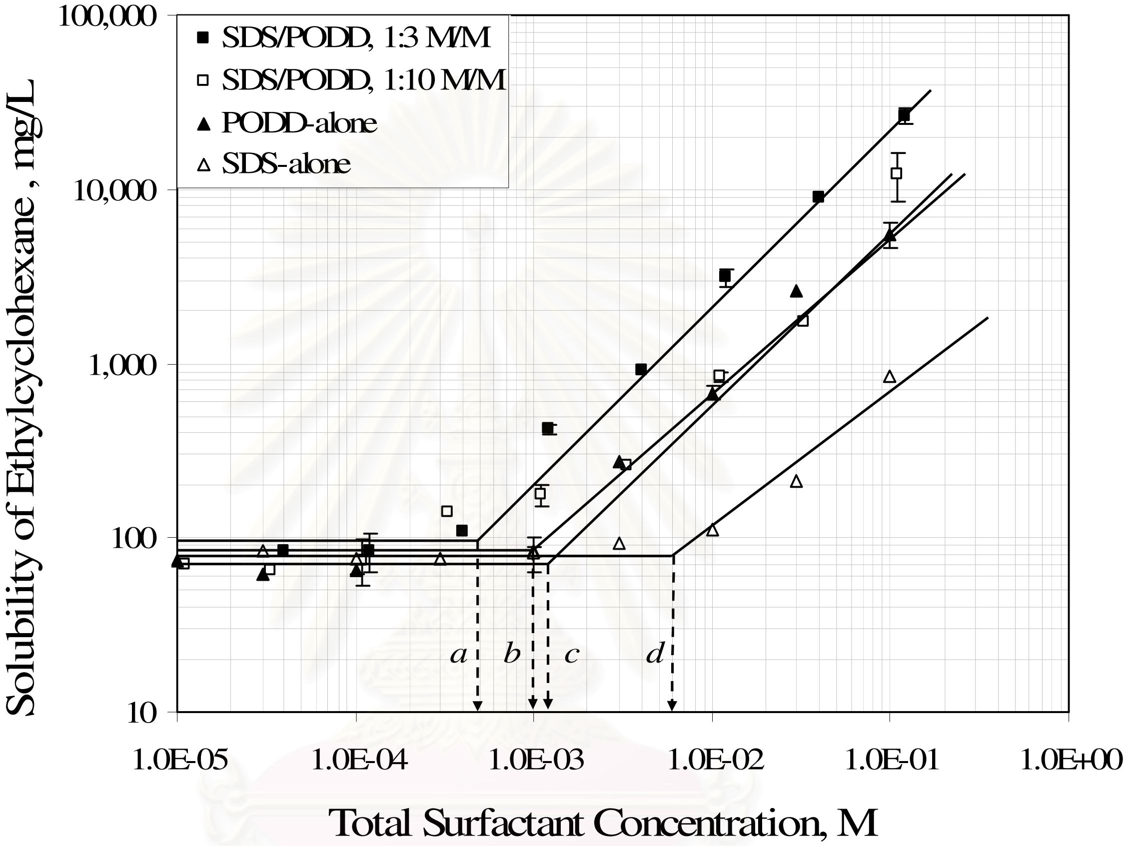


FIG. 4-10 Solubilization of ethylcyclohexane in SDS-alone, PODD-alone and in two SDS/PODD mixtures (0.01 M NaCl, 25°C). (*a* is the CMC of SDS/PODD; 1:3, *b* is the CMC of SDS/PODD, 1:10; *c* is the CMC of PODD-alone; and *d* is the CMC of SDS-alone).

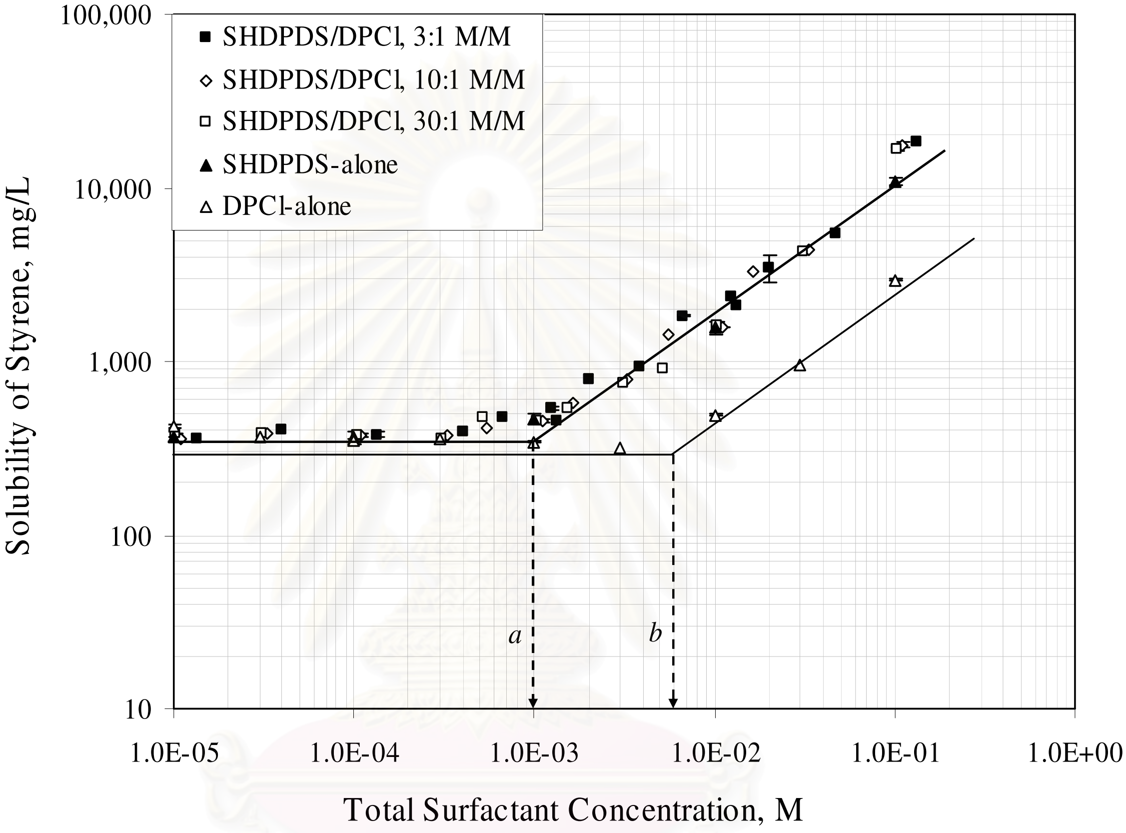


FIG. 4-11 Solubilization of styrene in sodium hexadecyl-diphenyloxide disulfonate (SHDPDS-alone), dodecylpyridinium chloride (DPCl-alone) and in three SHDPDS/DPCl mixtures (0.015 M NaCl, 25°C). *(a* is the CMC of SHDPDS-alone and the three SHDPDS/DPCl mixtures, and *b* is the CMC of DPCl-alone).

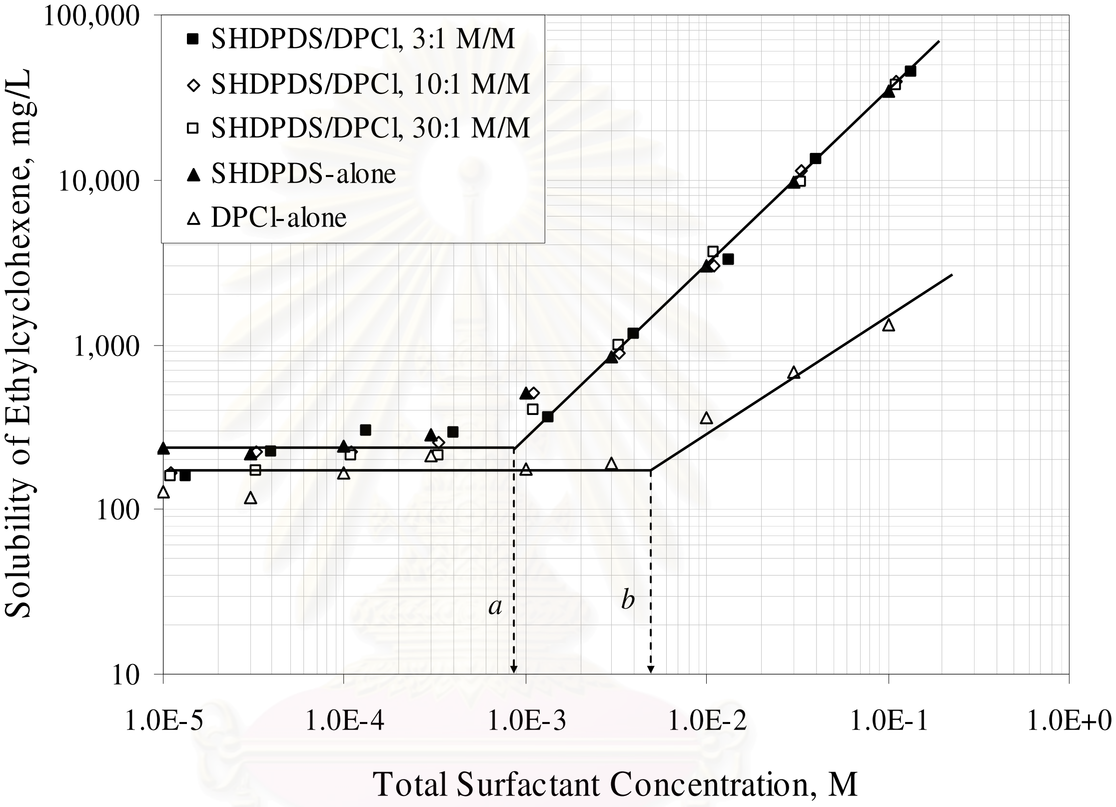


FIG. 4-12 Solubilization of ethylcyclohexane in SHDPDS-alone, DPCl-alone and in three SHDPDS/DPCl mixtures (0.015 M NaCl, 25°C). (*a* is the CMC of SHDPDS-alone and the three SHDPDS/DPCl mixtures, and *b* is the CMC of DPCl-alone).

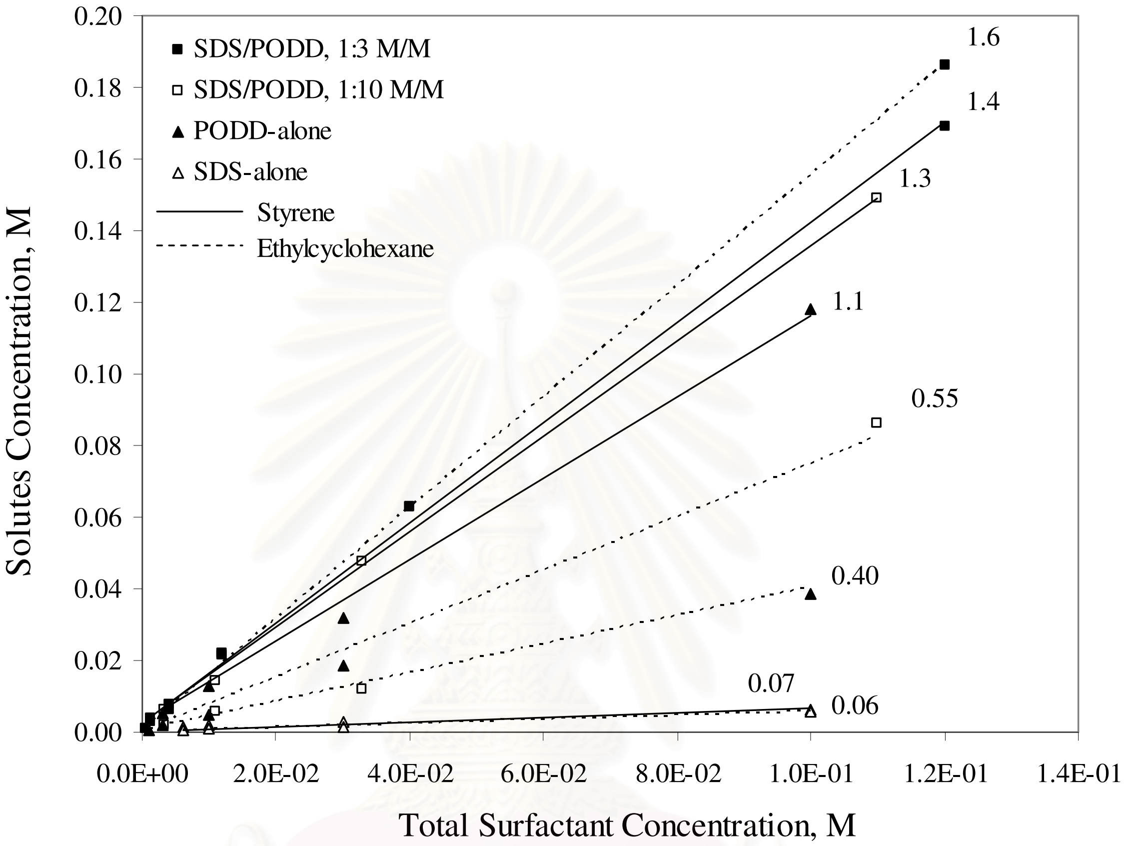


FIG. 4-13 Molar solubilization ratios MSRs of oils in mixed micelles of SDS/PODD, SDS-alone, and PODD-alone.

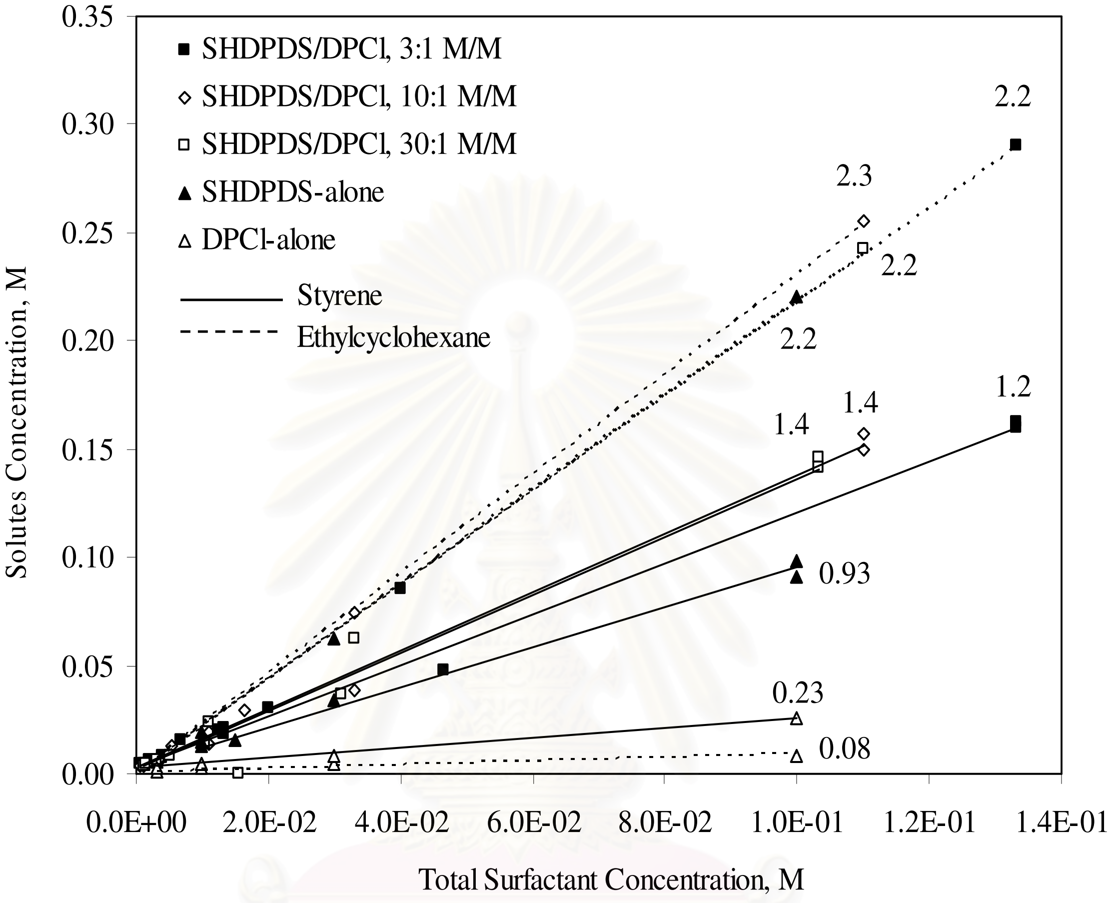


FIG. 4-14 MSRs of oils in mixed micelles of SHDPDS/DPCl and SHDPDS-alone and DPCl-alone.

TABLE 4-2 CMC, MSR, and K_{mic} values.

Surfactants	CMC, mM		MSR		K_{mic}		K_{adm}*	
	Styrene	Ethylcyclohexane	Styrene	Ethylcyclohexane	Styrene	Ethylcyclohexane	Styrene	Ethylcyclohexane
SDS/PODD, 1:3	0.50	0.50	1.4	1.6	0.12	0.60	0.26	0.16
SDS/PODD, 1:10	1.2	1.0	1.3	0.55	0.12	0.35	0.21	0.06
PODD-alone	1.4	1.2	1.1	0.40	0.11	0.28	0.19	0.06
SDS-alone	6.0	6.0	0.07	0.06	0.01	0.05	NM	NM
SHDPDS/DPCl, 3:1	0.80	0.80	1.2	2.2	0.11	0.68	0.35	0.75
SHDPDS/DPCl, 10:1	0.90	0.60	1.4	2.3	0.12	0.69	0.40	0.70
SHDPDS/DPCl, 30:1	1.1	0.70	1.4	2.2	0.12	0.68	NM	NM
SHDPDS-alone	1.0	0.80	0.93	2.2	0.10	0.68	0.40	0.65
DPCl-alone	6.0	5.0	0.23	0.08	0.04	0.07	NM	NM

* based on high X_{aq} values from Figure 4-16 to more closely reflect the maximum additivity method used to assess K_{mic}

NM: Not Measurable - Surfactant admicelle does not form because single surfactant and surface are like charged.

All SDS/PODD systems had 0.01M NaCl and all SHDPDS/DPCl syste,s had 0.015 M NaCl.

4.4 Adsolubilization in admicelles

Figure 4-15 and Table 4-3 show the admicellar partition coefficient, K_{adm}, versus the aqueous concentration of styrene for PODD-alone and for mixtures of PODD and SDS adsorbed onto silica. The first conclusion from this data is that, for any value of X_{aq}, the K_{adm} increases with increasing ratios of SDS/PODD. These results are consistent with the micellar solubilization results and help confirm our hypothesis that mixtures of anionic and cationic surfactants produce larger adsolubilization of organic compounds than single surfactant admicelles. A second observation from this data is that for a polar molecule like styrene, the value of K_{adm} plateaus with increasing aqueous molar fraction of the polar solute, suggesting a saturation of the palisade layer (Kitiyanan et al., 1996). This trend is observed for the PODD-alone and the SDS/PODD 1:10 admicelles. However, the K_{adm} values for the SDS/PODD 1:3 system, although higher, are independent at of X_{aq}. This behavior indicates that the surfactant-modified surface has an equal affinity for the styrene independent of the styrene concentration (i.e. K_{mic} is independent of styrene loading (X_{adm}) in the admicelle).

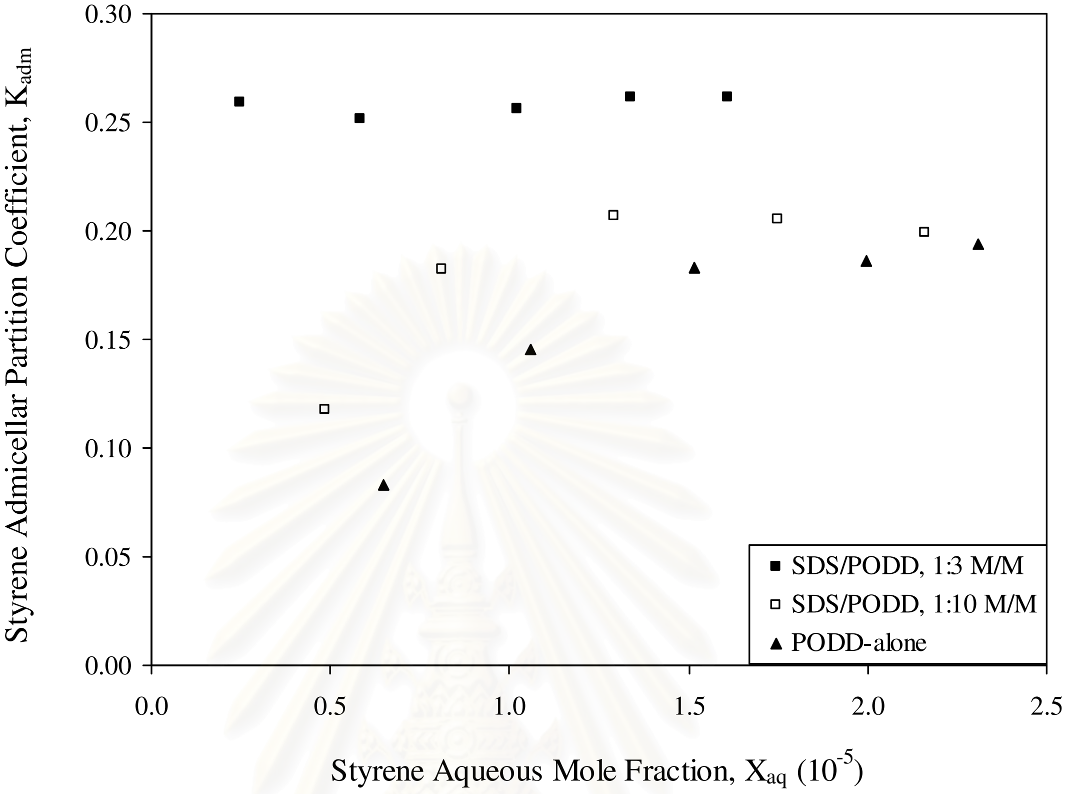


FIG. 4-15 Styrene admicellar partition coefficient, K_{adm}, in mixed SDS/PODD and PODD-alone admicelles on silica.

TABLE 4-3 Data for adsolubilization of styrene in mixed SDS/PODD and PODD-alone admicelles.

Ratio	S_i		S_f	S_i-S_f	A_i-A_f	C_i-C_f	X_{adm}	X_{aq}	K_{adm}	Mass of	CMC
(SDS/PODD)	ppm	mole/L	mole/L	mole/L	mole/L	mole/L		(10^{-5})		silica, g	mole/L
1:3 3.0E-03/9.0E-03 mole/L	100	8.70E-04	1.37E-04	7.33E-04	2.49E-03	8.27E-03	0.06	0.25	0.26	0.5	6.0E-04
	250	2.17E-03	3.24E-04	1.85E-03	2.49E-03	8.31E-03	0.15	0.58	0.25	0.5	
	500	4.35E-03	5.67E-04	3.78E-03	2.49E-03	8.20E-03	0.26	1.02	0.26	0.5	
	750	6.52E-03	7.44E-04	5.78E-03	2.49E-03	8.26E-03	0.35	1.34	0.26	0.5	
	1000	8.70E-03	8.94E-04	7.80E-03	2.49E-03	8.27E-03	0.42	1.61	0.26	0.5	
1:10 1.0E-03/1.0E-02 mole/L	100	8.70E-04	2.69E-04	6.01E-04	8.28E-04	9.11E-03	0.06	0.48	0.12	0.5	2.2E-03
	250	2.17E-03	4.52E-04	1.72E-03	8.21E-04	9.08E-03	0.15	0.81	0.18	0.5	
	500	4.35E-03	7.19E-04	3.63E-03	8.21E-04	9.10E-03	0.27	1.29	0.21	0.5	
	750	6.52E-03	9.71E-04	5.55E-03	8.25E-04	9.08E-03	0.36	1.75	0.21	0.5	
	1000	8.70E-03	1.20E-03	7.50E-03	8.31E-04	9.10E-03	0.43	2.16	0.20	0.5	
PODD-alone 1.0E-02 mole/L	100	8.70E-04	3.60E-04	5.10E-04	-	8.92E-03	0.05	0.65	0.08	0.5	2.3E-03
	250	2.17E-03	5.87E-04	1.59E-03	-	8.77E-03	0.15	1.06	0.15	0.5	
	500	4.35E-03	8.42E-04	3.51E-03	-	9.13E-03	0.28	1.52	0.18	0.5	
	750	6.52E-03	1.11E-03	5.42E-03	-	9.17E-03	0.37	1.99	0.19	0.5	
	1000	8.70E-03	1.28E-03	7.42E-03	-	9.15E-03	0.45	2.31	0.19	0.5	

Figure 4-16 and Table 4-4 show the admicellar partition coefficient of ethylcyclohexane, K_{adm}, as a function of ethylcyclohexane aqueous mole fraction in mixed SDS/PODD and PODD-alone admicelles. All the isotherms in Figure 4-14 have a positive slope which indicates that the adsolubilization process increases as additional solute partitions into the admicelles; this is as expected for a core solubilization process. And again the surfactant ratio of 1:3 is the most efficient in solubilizing ethylcyclohexane (has the largest K_{adm}), once again supporting our hypothesis of improved adsolubilization as the mixed system approaches equimolar conditions.

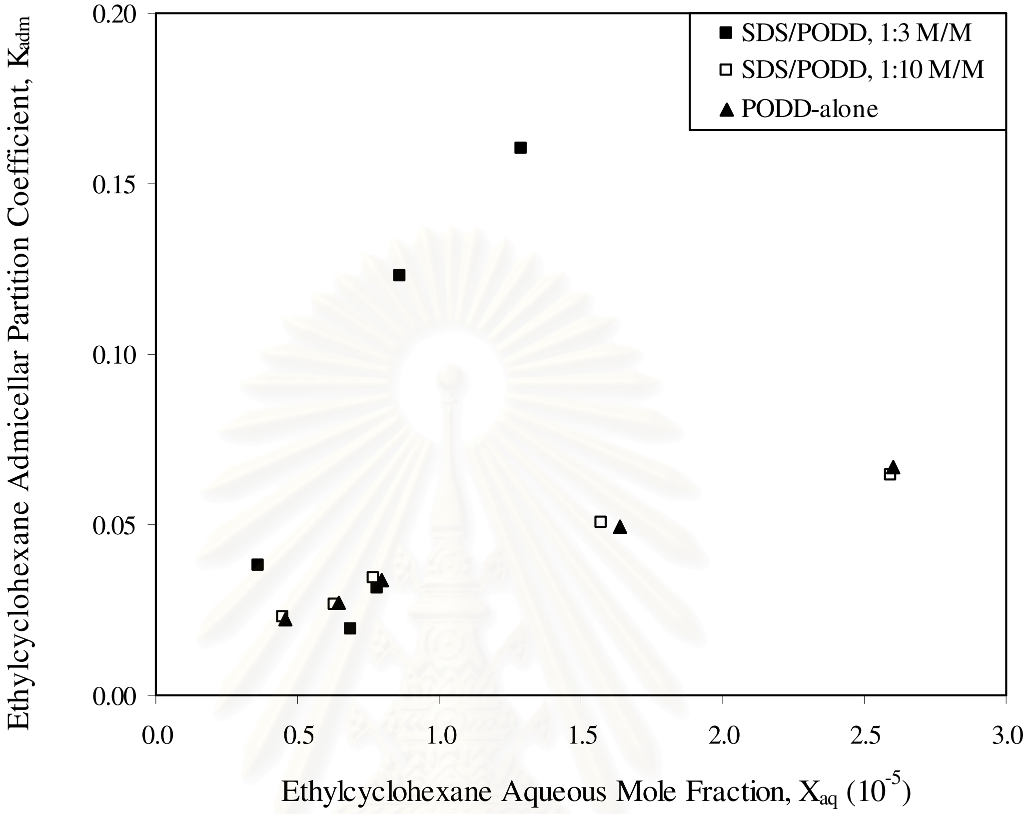


FIG. 4-16 Ethylcyclohexane adicellar partition coefficient, K_{adm}, in mixed SDS/PODD and PODD-alone admicelles on silica.

TABLE 4-4 Data for adsolubilization of ethylcyclohexane in mixed SDS/PODD and PODD-alone admicelles.

Ratio	S_i		S_f	S_i-S_f	A_i-A_f	C_i-C_f	X_{adm}	X_{aq}	K_{adm}	Mass of	CMC
(SDS/PODD)	ppm	mole/L	mole/L	mole/L	mole/L	mole/L		(10^{-5})		silica, g	mole/L
1:3 3.0E-03/9.0E-03 mole/L	50	3.51E-04	2.02E-04	1.49E-04	2.48E-03	8.22E-03	0.01	0.36	0.04	0.5	6.0E-04
	75	5.27E-04	3.83E-04	1.44E-04	2.49E-03	8.25E-03	0.01	0.69	0.02	0.5	
	100	7.02E-04	4.34E-04	2.68E-04	2.49E-03	8.21E-03	0.02	0.78	0.03	0.5	
	250	1.76E-03	4.81E-04	1.27E-03	2.49E-03	8.24E-03	0.11	0.87	0.12	0.5	
	500	3.51E-03	7.15E-04	2.80E-03	2.49E-03	8.29E-03	0.21	1.29	0.16	0.5	
1:10 1.0E-03/1.0E-02 mole/L	50	3.51E-04	2.48E-04	1.03E-04	7.35E-04	9.25E-03	0.01	0.45	0.02	0.5	2.2E-03
	75	5.27E-04	3.50E-04	1.76E-04	7.38E-04	9.57E-03	0.02	0.63	0.03	0.5	
	100	7.02E-04	4.27E-04	2.75E-04	7.17E-04	9.47E-03	0.03	0.77	0.03	0.5	
	250	1.76E-03	8.72E-04	8.84E-04	7.50E-04	9.46E-03	0.08	1.57	0.05	0.5	
	500	3.51E-03	1.44E-03	2.07E-03	7.37E-04	9.58E-03	0.17	2.59	0.06	0.5	
PODD-alone 1.0E-02 mole/L	50	3.51E-04	2.52E-04	9.89E-05	-	9.59E-03	0.01	0.45	0.02	0.5	2.3E-03
	75	5.27E-04	3.57E-04	1.69E-04	-	9.52E-03	0.02	0.64	0.03	0.5	
	100	7.02E-04	4.43E-04	2.60E-04	-	9.46E-03	0.03	0.80	0.03	0.5	
	250	1.76E-03	9.10E-04	8.45E-04	-	9.54E-03	0.08	1.64	0.05	0.5	
	500	3.51E-03	1.45E-03	2.07E-03	-	9.78E-03	0.17	2.60	0.07	0.5	

Figure 4-17 and Table 4-5 shows the admicellar partition coefficient of styrene, K_{adm}, as a function of styrene aqueous mole fraction in mixed SHDPDS/DPCl and SHDPDS-alone admicelles. The values of K_{adm} are higher at low X_{aq} values and plateau towards a minimum value at higher X_{aq}. This suggests preferential adsolubilization at lower loading (lower X_{aq} and X_{adm}) and eventual site saturation with increased loading (ie, the palisade layer effect described above). It should be noted that the preferential adsolubilization at lower values of X_{aq} diminishes with increasing ratios of SHDPDS/DPCl: this can again be attributed to the "squeezing out" phenomenon mentioned above (i.e. the co-surfactant is filling spaces that might have been filled by the solute, thereby diminishing the palisade effect).

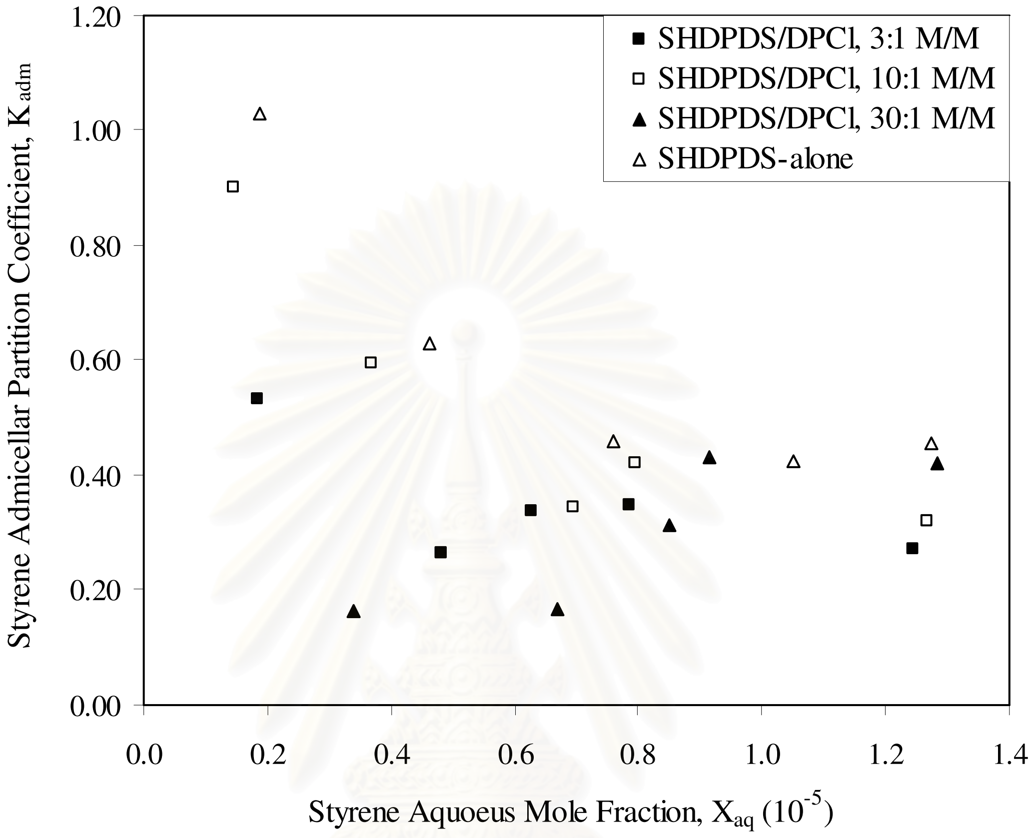


FIG. 4-17 Styrene admicellar partition coefficient, K_{adm}, in mixed SHDPDS/DPCl and SHDPDS-alone on alumina.

TABLE 4-5 Data for adsolubilization of styrene in mixed SHDPDS/DPCl and SHDPDS-alone admicelles.

Ratio	S_i		S_f	S_i-S_f	A_i-A_f	C_i-C_f	X_{adm}	X_{aq}	K_{adm}	Mass of	CMC
(SHDPDS/DPCl)	ppm	mole/L	mole/L	mole/L	mole/L	mole/L		(10^{-5})		alumina, g	mole/L
3:1 1.0E-03/3.33E-04 mole/L	25	2.17E-04	1.02E-04	1.15E-04	7.41E-04	3.18E-04	0.10	0.18	0.53	0.1	5.5E-04
	50	4.35E-04	2.68E-04	1.67E-04	8.08E-04	3.24E-04	0.13	0.48	0.27	0.1	
	75	6.52E-04	3.49E-04	3.04E-04	8.18E-04	3.18E-04	0.21	0.63	0.34	0.1	
	100	8.70E-04	4.37E-04	4.33E-04	8.23E-04	3.20E-04	0.27	0.79	0.35	0.1	
	150	1.30E-03	6.92E-04	6.13E-04	8.81E-04	3.18E-04	0.34	1.25	0.27	0.1	
10:1 1.0E-03/1.0E-04 mole/L	25	2.17E-04	8.16E-05	1.36E-04	7.90E-04	1.00E-04	0.13	0.15	0.90	0.1	4.3E-04
	50	4.35E-04	2.04E-04	2.31E-04	7.27E-04	1.00E-04	0.22	0.37	0.59	0.1	
	75	6.52E-04	3.86E-04	2.67E-04	7.48E-04	1.00E-04	0.24	0.69	0.34	0.1	
	100	8.70E-04	4.41E-04	4.28E-04	7.58E-04	1.00E-04	0.33	0.79	0.42	0.1	
	150	1.30E-03	7.03E-04	6.01E-04	7.91E-04	1.00E-04	0.40	1.27	0.32	0.1	
30:1 1.0E-03/3.33E-05 mole/L	25	2.17E-04	1.88E-04	2.90E-05	4.64E-04	3.33E-05	0.06	0.34	0.16	0.1	5.5E-04
	50	4.35E-04	3.71E-04	6.37E-05	4.79E-04	3.33E-05	0.11	0.67	0.17	0.1	
	75	6.52E-04	4.72E-04	1.80E-04	4.63E-04	3.33E-05	0.27	0.85	0.31	0.1	
	100	8.70E-04	5.09E-04	3.61E-04	5.18E-04	3.33E-05	0.40	0.92	0.43	0.1	
	150	1.30E-03	7.13E-04	5.92E-04	4.73E-04	3.33E-05	0.54	1.28	0.42	0.1	
SHDPDS-alone 1.0E-03 mole/L	25	2.17E-04	1.04E-04	1.14E-04	4.79E-04	-	0.19	0.19	1.03	0.1	4.9E-04
	50	4.35E-04	2.57E-04	1.78E-04	4.33E-04	-	0.29	0.46	0.63	0.1	
	75	6.52E-04	4.21E-04	2.31E-04	4.33E-04	-	0.35	0.76	0.46	0.1	
	106	9.23E-04	5.83E-04	3.39E-04	4.20E-04	-	0.45	1.05	0.43	0.1	
	150	1.30E-03	7.07E-04	5.98E-04	4.33E-04	-	0.58	1.27	0.46	0.1	

Figure 4-18 and Table 4-6 show the admicellar partition coefficient of ethylcyclohexane, K_{adm}, as a function of ethylcyclohexane aqueous mole fraction in mixed SHDPDS/DPCl and SHDPDS-alone admicelles. The curves in Figure 4-18 resemble the curves in Figure 4-16 in that the slopes of the curves are positive and that the values of the admicelle partition coefficients are larger for the mixed system SHDPDS/DPCl at the highest mole ratio 3:1. Once again these results illustrate the more hydrophobic nature of the mixed admicelle and corroborate our hypothesis. In the case of ethylcyclohexane, admicelles formulated with mixtures of anionic and cationic surfactants show larger solubilization than single SHDPDS systems, even though this is not observed in the case of micelles: this disparity could be due to the two-dimensional nature of admicelles versus the three-dimensional nature of micelles (i.e. the packing synergy may be better exploited in more planar structures).

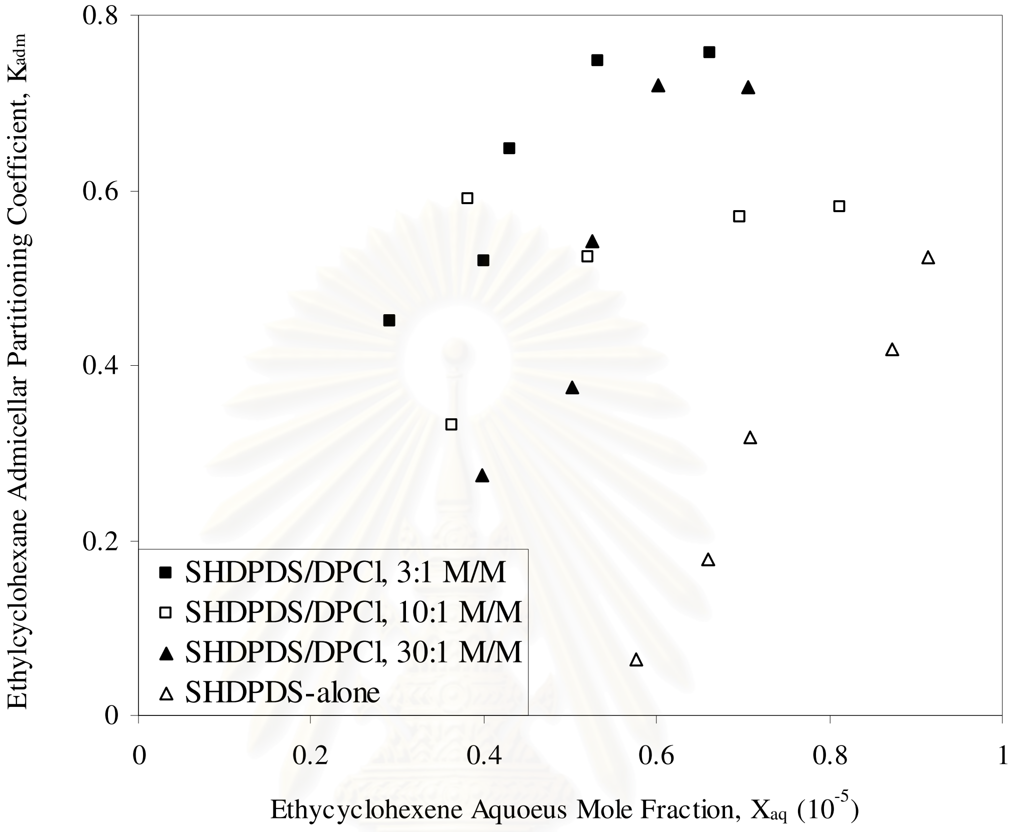


FIG. 4-18 Ethylcyclohexane admicellar partition coefficient, K_{adm}, in mixed SHDPDS/DPCl and SHDPDS-alone.

TABLE 4-6 Data for adsolubilization of ethylcyclohexane in mixed SHDPDS/DPCl and SHDPDS-alone admicelles.

Ratio (SHDPDS/DPCl)	S_i		S_f	S_i-S_f	A_i-A_f	C_i-C_f	X_{adm}	X_{aq}	K_{adm}	Mass of	CMC
	ppm	mole/L	mole/L	mole/L	mole/L	mole/L		(10^{-5})		alumina, g	mole/L
3:1 1.0E-03/3.33E-04 mole/L	46	3.23E-04	1.61E-04	1.61E-04	8.23E-04	2.47E-04	0.13	0.29	0.45	0.1	5.5E-04
	69	4.84E-04	2.23E-04	2.61E-04	7.52E-04	2.42E-04	0.21	0.40	0.52	0.1	
	92	6.45E-04	2.39E-04	4.06E-04	8.12E-04	2.42E-04	0.28	0.43	0.65	0.1	
	138	9.68E-04	2.96E-04	6.72E-04	7.87E-04	2.27E-04	0.40	0.53	0.75	0.1	
	184	1.29E-03	3.67E-04	9.23E-04	6.80E-04	2.45E-04	0.50	0.66	0.76	0.1	
10:1 1.0E-03/1.0E-04 mole/L	46	3.23E-04	2.02E-04	1.20E-04	7.89E-04	8.83E-05	0.12	0.36	0.33	0.1	4.3E-04
	69	4.84E-04	2.12E-04	2.72E-04	8.46E-04	9.05E-05	0.23	0.38	0.59	0.1	
	92	6.45E-04	2.89E-04	3.56E-04	8.59E-04	8.83E-05	0.27	0.52	0.52	0.1	
	138	9.68E-04	3.87E-04	5.81E-04	7.91E-04	9.57E-05	0.40	0.70	0.57	0.1	
	184	1.29E-03	4.52E-04	8.39E-04	8.46E-04	9.05E-05	0.47	0.81	0.58	0.1	
30:1 1.0E-03/3.33E-05 mole/L	46	3.23E-04	2.22E-04	1.01E-04	7.89E-04	3.33E-05	0.11	0.40	0.27	0.1	4.3E-04
	69	4.84E-04	2.79E-04	2.05E-04	8.46E-04	3.33E-05	0.19	0.50	0.38	0.1	
	92	6.45E-04	2.92E-04	3.54E-04	8.59E-04	3.33E-05	0.28	0.52	0.54	0.1	
	138	9.68E-04	3.35E-04	6.33E-04	7.91E-04	3.33E-05	0.43	0.60	0.72	0.1	
	184	1.29E-03	3.92E-04	8.99E-04	8.46E-04	3.33E-05	0.51	0.71	0.72	0.1	
SHDPDS-alone 1.0E-03 mole/L	50	3.53E-04	3.20E-04	3.26E-05	8.49E-04	-	0.04	0.58	0.06	0.1	4.9E-04
	69	4.84E-04	3.67E-04	1.17E-04	8.74E-04	-	0.12	0.66	0.18	0.1	
	92	6.45E-04	3.93E-04	2.52E-04	8.70E-04	-	0.22	0.71	0.32	0.1	
	138	9.68E-04	4.85E-04	4.83E-04	8.39E-04	-	0.37	0.87	0.42	0.1	
	184	1.29E-03	5.08E-04	7.83E-04	8.53E-04	-	0.48	0.91	0.52	0.1	

To compare the values of K_{adm} reported in this section with K_{mic} values reported above we will focus on the K_{adm} values at higher levels of X_{aq} as this more closely mimics the maximum additivity method used to determine K_{mic}. By comparing the K_{adm} and K_{mic} values in Table 4-2, it is interesting to note that for the SDS/PODD system, the admicelles are more efficient in solubilizing styrene than are the micelles - again this may be attributed to the more planar structure of admicelles favoring the palisade effect. Conversely, the SDS/PODD admicelles are less efficient for ethylcyclohexane - albeit from Figure 4-16 we observe that the isotherm is continuing to rise and since it was not possible to conduct experiments at higher levels, we may not have realized the maximum value. For the SHDPDS/DPCl system, we observe that once again the admicelles are more efficient for incorporating styrene, while the micelles and admicelles are equally effective for ethylcyclohexane (see Charoensaeng (2003) for details of SHDPDS/DPCl experiments). Thus, we observe that the relative efficiency of admicelles and micelles is a function of the surfactants and their mole ratio in the mixture and the solute of interest.

4.5 Column experiments

Column experiments were conducted to evaluate the behavior of both surfactants and organic solutes in continuous flow systems, as discussed below (data is shown in Krajangpan, 2004).

4.5.1 Surfactants behavior in column study

The surfactant breakthrough curves of PODD-alone and mixed SDS/PODD, 1:3 ratio (both with styrene and ethylcyclohexane studies) with silica were analyzed for surfactant breakthrough. The bar graphs in Figure 4-19 show the adsorption of surfactants in the column before and after water flushing through the column. We found that for the mixed SDS/PODD, 1:3 ratio, the surfactant adsorption of styrene study was similar to the surfactant adsorption of ethylcyclohexane study and less surfactant desorbed than for the single surfactant case for both oils study. For the PODD-alone, the surfactant adsorption of styrene and ethylcyclohexane studies was similar and less than that of the mixed SDS/PODD, 1:3 ratio, while the surfactant desorption in the PODD-alone was less than that of the mixed SDS/PODD, 1:3 ratio. It means that the admicelles of the mixed SDS/PODD, 1:3 ratio, can adsorb more on silica surface and are more stable.

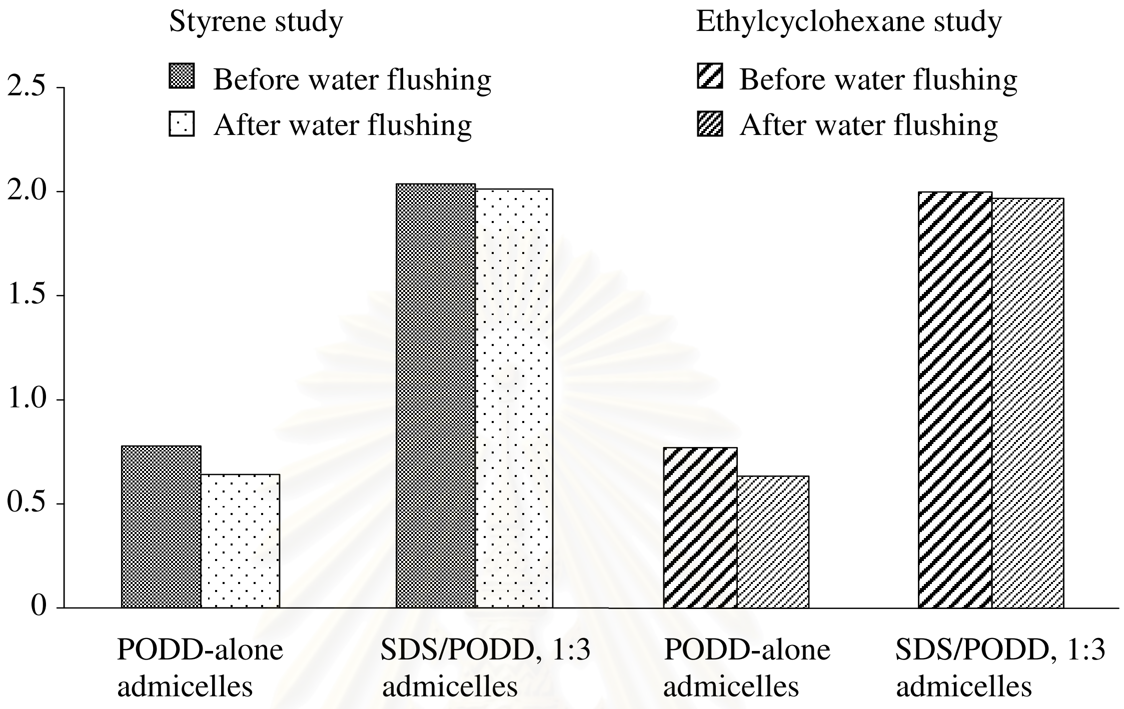


FIG. 4-19. Column experiments, surfactants adsorption while flowing through silica with PODD-alone admicelles, and silica with SDS/PODD, 1:3, admicelles, in styrene and ethylcyclohexane experiments.

4.5.2 Retardation of styrene and ethylcyclohexane in column study

Figure 4-20 shows styrene retardation factors of 1.7, 4.0, and 12.8 for silica without admicelles, for silica with PODD-alone admicelles, and for silica with SDS/PODD, 1:3 ratio, respectively. Figure 4-21 shows ethylcyclohexane retardation factors of 1.3, 32.1, and 90.2 while flowing through silica without admicelles, silica with PODD-alone admicelles, and silica with SDS/PODD, 1:3 ratio, respectively. We found that both styrene and ethylcyclohexane have about 3 times higher retardation while flowing through the silica with mixed SDS/PODD at 1:3 ratio than for the silica with PODD-alone admicelles. The retardation of ethylcyclohexane while flowing through the silica with mixed SDS/PODD, 1:3 ratio, is about 7 times higher than that of styrene. This result confirms the adsolubilization experiments of ethylcyclohexane in the admicelles of mixed SDS/PODD, 1:3 ratio, which is greater than that of styrene in the same kind admicelles (Fuangswasdi et al., 2005b).

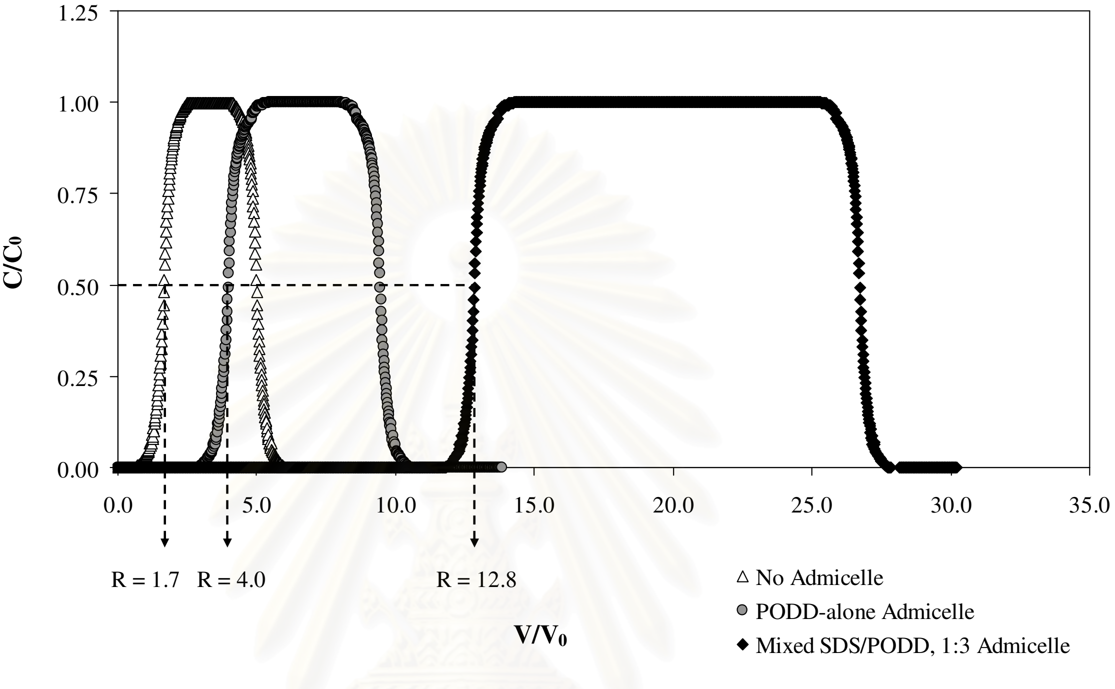


FIG. 4-20. Styrene retardation while flowing through silica without admicelles (R = 1.7), silica with PODD-alone admicelles (R = 4.0), and silica with SDS/PODD, 1:3 ratio admicelles (R = 12.8) (0.01 M NaCl, 25°C).

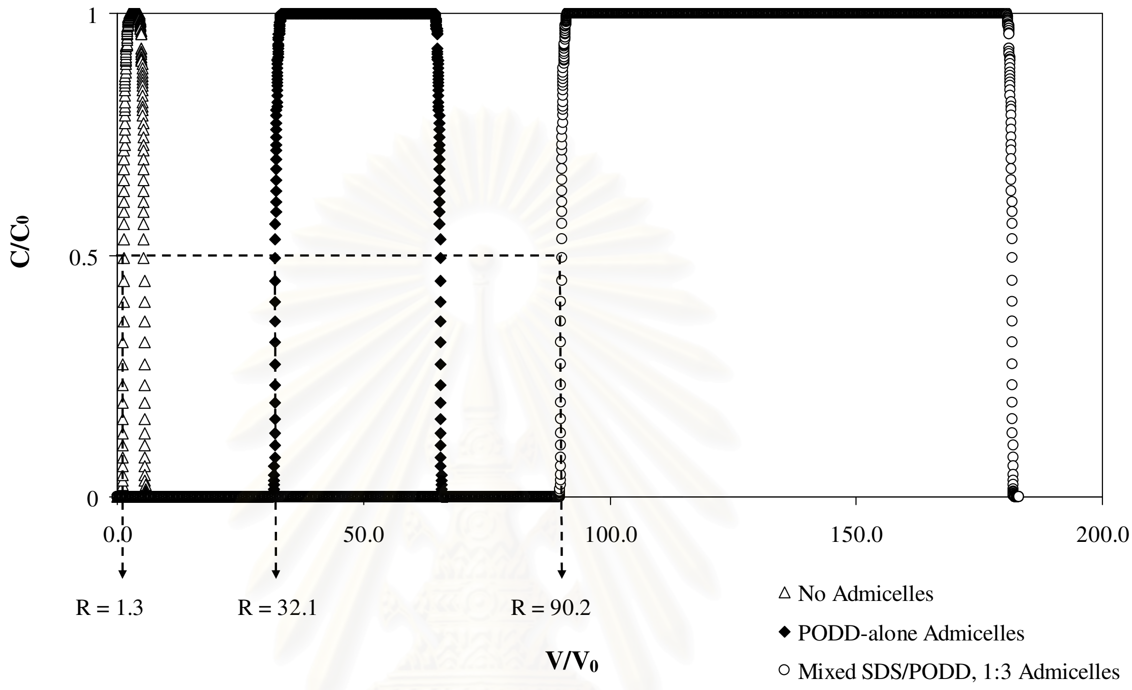


FIG. 4-21. Ethylcyclohexane retardation while flowing through silica without admicelles (R = 1.3), silica with PODD-alone admicelles (R = 32.1), and silica with SDS/PODD, 1:3 ratio admicelles (R = 90.2) (0.01 M NaCl, 25°C).

Figure 4-22 compares the adsorption of styrene and ethylcyclohexane while flowing through silica without admicelles, silica with PODD-alone admicelles, and silica with SDS/PODD, 1:3 ratio, admicelles in the column (in units of mole/g of silica). We found that both solutes were adsorbed more on the mixed-surfactant admicelles than on the other surfaces. We also found that ethylcyclohexane was adsorbed by the PODD-alone admicelles and mixed SDS/PODD, 1:3 ratio, admicelles on silica surface more than was the styrene. Conversely, the silica without admicelles had no effect to ethylcyclohexane over styrene.

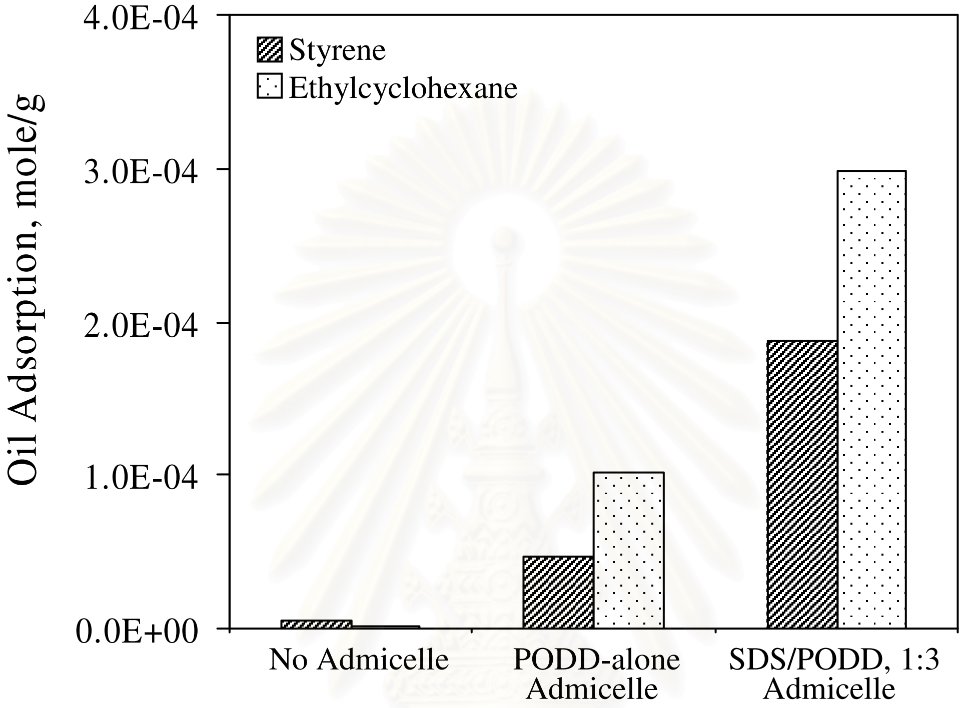


FIG. 4-22. Column experiments, styrene and ethylcyclohexane adsorption while flowing through silica without admicelles, silica with PODD-alone admicelles, and silica with SDS/PODD, 1:3 ratio admicelles (0.01 M NaCl, 25°C).

4.6 Admicelle stability in batch experiments.

Figure 4-23 shows the surfactant adsorption of silica with PODD-alone admicelles and mixed SDS/PODD, 1:3 ratio, admicelles. We found that after water flushing for five times, the admicelles of PODD-alone and mixed SDS/PODD, 1:3 ratio desorbed from the adsorbent in nearly the same percentage, 41.8% and 39.1%, respectively. In addition, the admicelles of mixed SDS/PODD, 1:3 ratio, were still adsorbed on silica surface higher than PODD-alone admicelles (3.7 x 10^{-4} mole/g and 2.3 x 10^{-4} mole/g, respectively). The anionic and cationic surfactant in mixed SDS/PODD, 1:3 ratio, approached equimolar after five times of water flushing. In addition, we found that in the batch experiments the admicelles desorbed significantly from the adsorbent while in the column experiments the desorption of admicelles was much less.

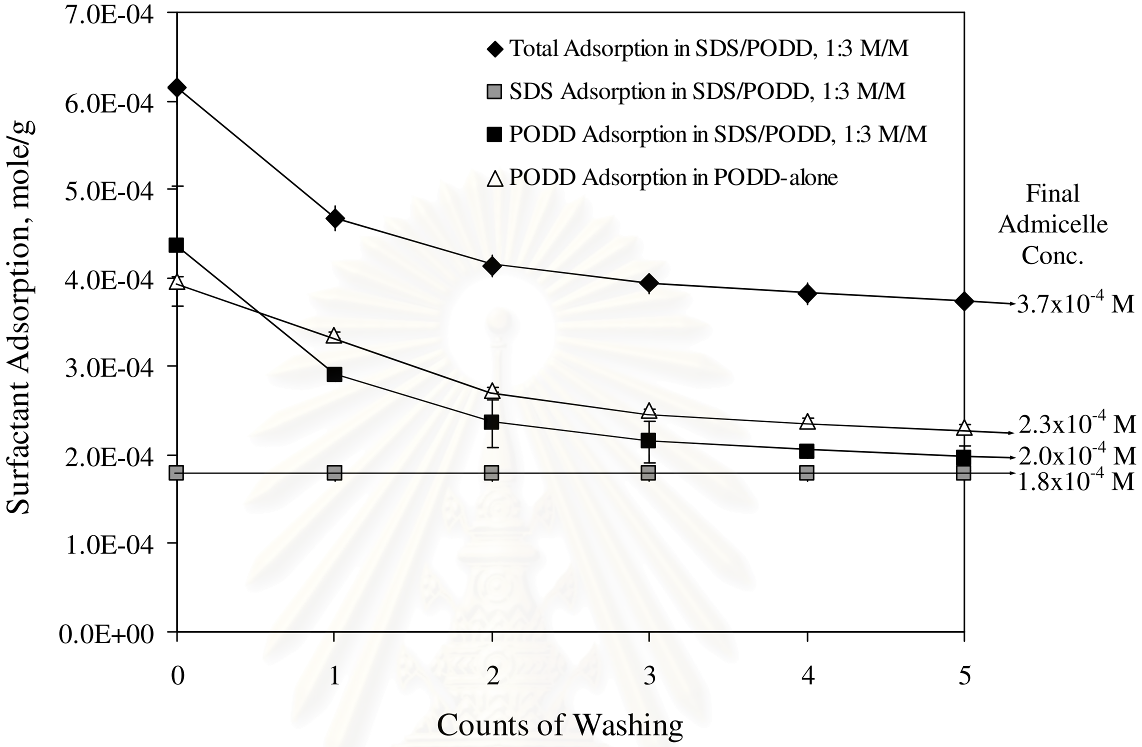


FIG. 4-23. Column experiments, surfactant adsorption before and after water flushing (0.01 M NaCl, 25°C).

4.7 Surface Tension Experiments

The results of surface tension of mixed SDS/PODD in 1:3 ratio, PODD-alone, and SDS-alone are shown in Table 4-7 and Figure 4-24. Figure 4-25 and Table 4-8 show the saturation adsorption and the minimum coverage area of surfactant molecules of mixed SDS/PODD (1:3 ratio), PODD-alone, and SDS-alone from surface tension experiments. Table 4-9 shows the minimum coverage area of mixed SDS/PODD (1:3 ratio) and PODD-alone on silica surface from the previous work, adsorption experiments. The minimum coverage area of mixed SDS/PODD (1:3 ratio) which forms monolayer from the surface tension experiment (see Table 4-8) covers the area 0.70 nm^2/molecule, while the minimum coverage area of mixed SDS/PODD (1:3 ratio) which forms admicelle from the adsorption isotherm experiment (see Table 4-9) covers the area 0.36 nm^2/molecule. We can see that the coverage area of monolayer is about 2 times larger than that of the bilayer or the admicelle. When the surfactant molecules form admicelles or double layer on silica surface, the minimum coverage area of the molecules is expected to be (0.70 nm^2/molecule/2 molecules) 0.35 nm^2/molecule. The minimum coverage area of the SDS/PODD (1:3, ratio) from the adsorption experiment is 0.36 nm^2/molecule. The study of SEM and TEM will show the size of the silica absorbent with admicelles adsorbed on the surface compares to the silica particles without admicelles. Table 4-8 also shows the minimum coverage area of PODD-alone monolayer from surface tension experiment 0.59 nm^2/molecule, while Table 4-9 shows the minimum coverage area of PODD-alone admicelle from adsorption experiment 0.56 nm^2/molecule. We can see that when PODD-alone forms admicelle, it performs nearly the same of minimum coverage area as when it forms monolayer. Thus, it is obviously shown that PODD-alone molecules do not pack as efficiently when it becomes admicelles as the mixed surfactant do. Then mixed surfactant can have more adsolubilization than the surfactant-alone because of the denser molecules.

TABLE 4-7 Surface tension data for mixed SDS/PODD, PODD-alone, and SDS-alone (0.01 M NaCl, 30^{o}C).

SDS/PADD, 1:3		PADD-alone		SDS-alone	
Concentration M	Surface Tension mN/m	Concentration M	Surface Tension mN/m	Concentration M	Surface Tension mN/m
1.00E-03	26.1	1.00E-05	58.3	1.00E-03	45.1
7.00E-04	26.2	1.00E-04	35.9	1.00E-02	37.4
5.00E-04	26.2	1.00E-03	36.5	4.00E-04	49.7
2.00E-03	26.6	1.00E-02	39.9	5.00E-03	37.1
7.00E-05	26.9	8.00E-05	38.0	1.00E-03	44.3
1.00E-04	27.3	5.00E-05	40.7	1.50E-03	42.8
1.50E-04	26.7	3.00E-04	34.6	2.00E-03	39.7
3.00E-04	26.2	5.00E-04	35.8	8.00E-04	46.6
4.00E-04	26.0	8.00E-04	36.3	2.50E-03	36.1
1.00E-05	36.3	3.00E-05	44.7	4.00E-03	34.7
4.00E-05	28.1	1.50E-04	35.2	5.00E-03	36.6
7.00E-06	39.5	2.00E-04	34.8	2.00E-02	36.6
2.00E-05	33.4	-	-	1.76E-03	42.0
3.00E-05	30.6	-	-	2.20E-03	39.3
5.00E-05	27.9	-	-	6.00E-03	37.2
1.50E-05	32.2	-	-	3.00E-03	35.9
2.50E-05	29.6	-	-	3.50E-03	33.7

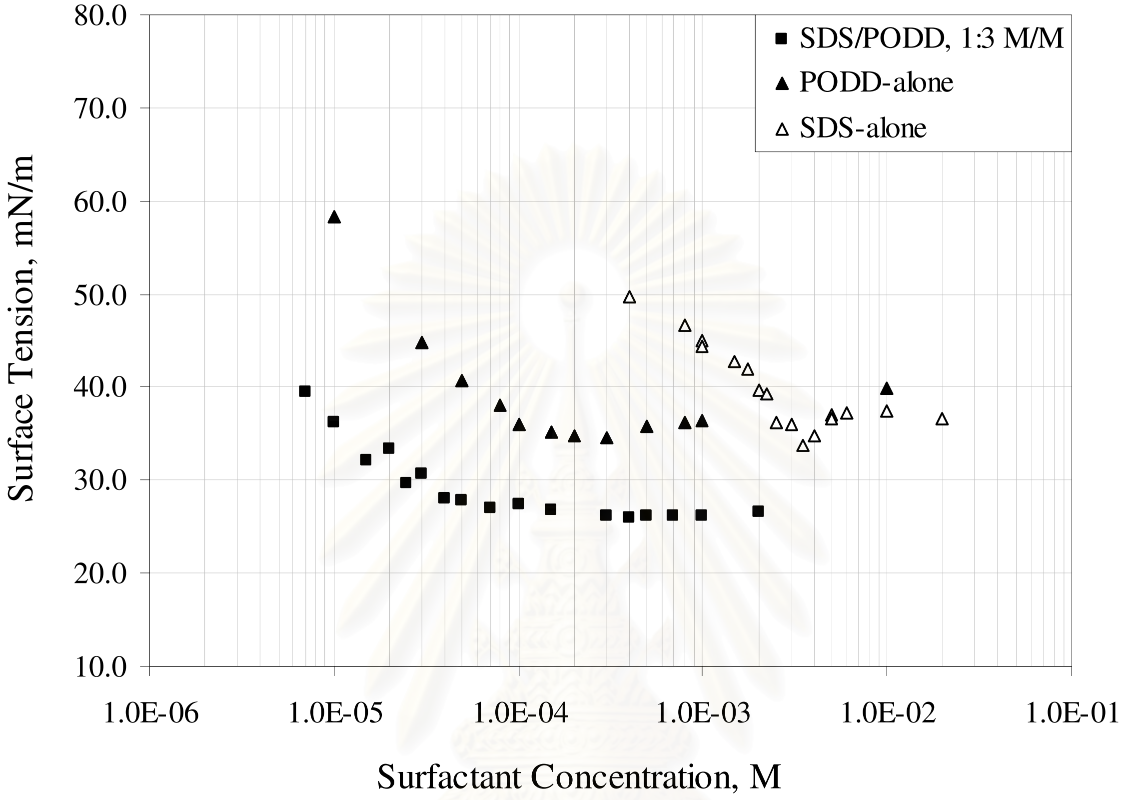


FIG. 4-24 Surface tension study of mixed SDS/PODD, PODD-alone, and SDS-alone (0.01 M NaCl, 30^{o}C).

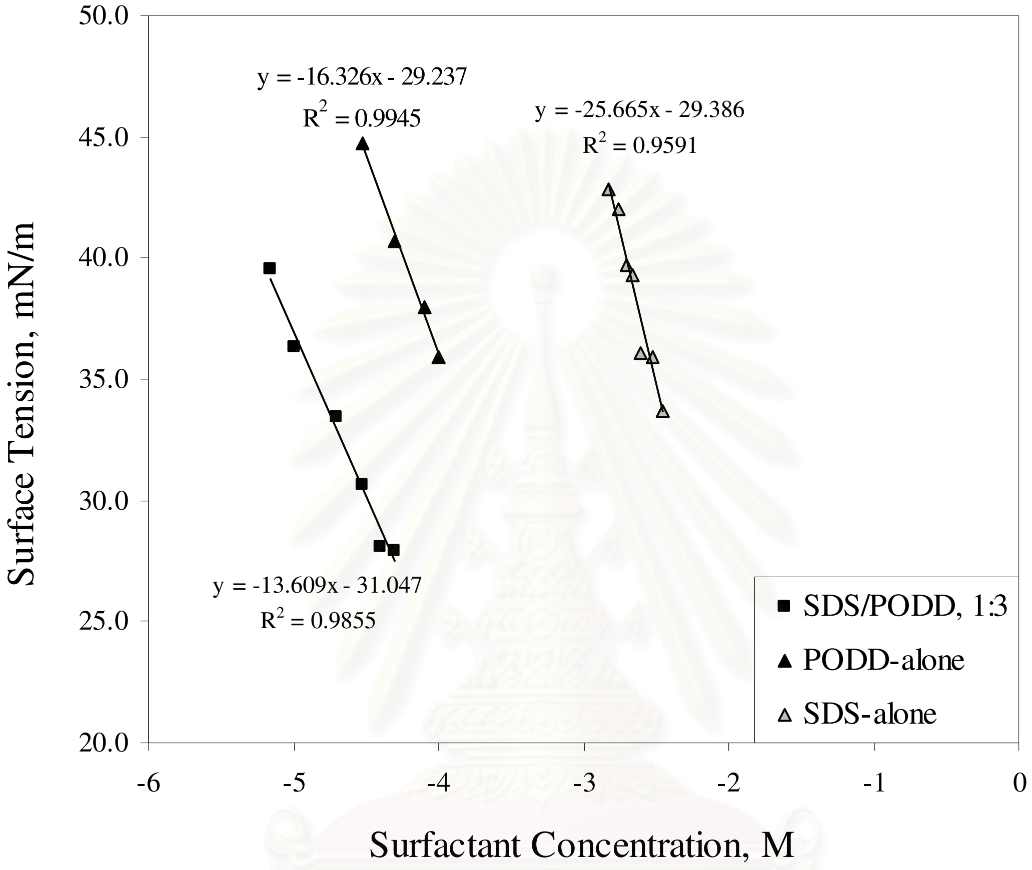


FIG. 4-25 Surface tension study of mixed SDS/PODD, PODD-alone, and SDS-alone (0.01 M NaCl, 30°C).

TABLE 4-8 The saturation adsorption and the minimum coverage area of surfactant molecules of mixed SDS/PODD, PODD-alone, and SDS-alone from surface tension.

Ratio	Slope	Saturation adsorption Γ, mole/m^2	Minimum Coverage Area A_{min}, nm^2/molecule
SDS/PODD, 1:3	-13.75	2.37E-06	0.70
PODD-alone	-16.33	2.81E-06	0.59
SDS-alone	-25.67	4.42E-06	0.38

TABLE 4-9 The minimum coverage area of mixed SDS/PODD and PODD-alone on silica surface from adsorption.

Medium	Ratio	Plateau Adsorption									Plateau Aqueous Surfactant Concentration M
		Cationic Surfactant			Anionic Surfactant			Total Surfactant			
		molecules/ nm^2	nm^2/ molecule	mole/g	molecules/ nm^2	nm^2/ molecule	mole/g	molecules/ nm^2	nm^2/ molecule	mole/g	
Silica	SDS/PODD, 1:3	2.8	0.36	6.63E-04	1.2	0.83	2.84E-04	4	0.25	9.47E-04	0.50
	PODD-alone	1.8	0.56	4.26E-04	NA	NA	NA	1.8	0.56	4.26E-04	1.40

NA - Not Applicable - The adsorption of like-charged surfactant alone and media was below detection limits.

4.8 Electron Microscope Studies

4.8.1 SEM (Scanning Electron Microscopy)

Figure 4-26 shows the particles of silica without admicelles adsorbed (Figure 4-26 (a)) on the surface as compared to the adsorbent with mixed SDS/PODD admicelles and PODD-alone admicelles adsorbed on the surface (Figure 4-26 (b) and Figure 4-26 (c), respectively). From the Figure 4-26 (a), the average size of silica particles diameter is approximately 50 nm, while from Figure 4-26 (b) and Figure 4-26 (c) the average size of the particle diameter is nearly the same, roughly 65 nm. This indicates that surfactant-modified silica with mixed SDS/PODD (1:3, ratio) or PODD-alone adsorbed on the surface increases the particle size by roughly 30%. This would suggest that the thickness of the admicelle on the silica is approximately (65 nm - 50 nm)/ 2 or 7.5 nm, which is consistent with a bilayer of surfactant molecules and at least 2 or 3 monomers of styrene. Molar solubilization ratio (MSR) data from Figure 4-13 shows that 1 molecule of the surfactant can adsorb 1.4 molecules of styrene monomers. Thus, a bilayer (admicelle) can adsorb about 3 (2.8) styrene monomers. Thus, the thickness of the admicelle is estimated by 2 surfactant molecules and 3 styrene monomers (see Figure 4-27).

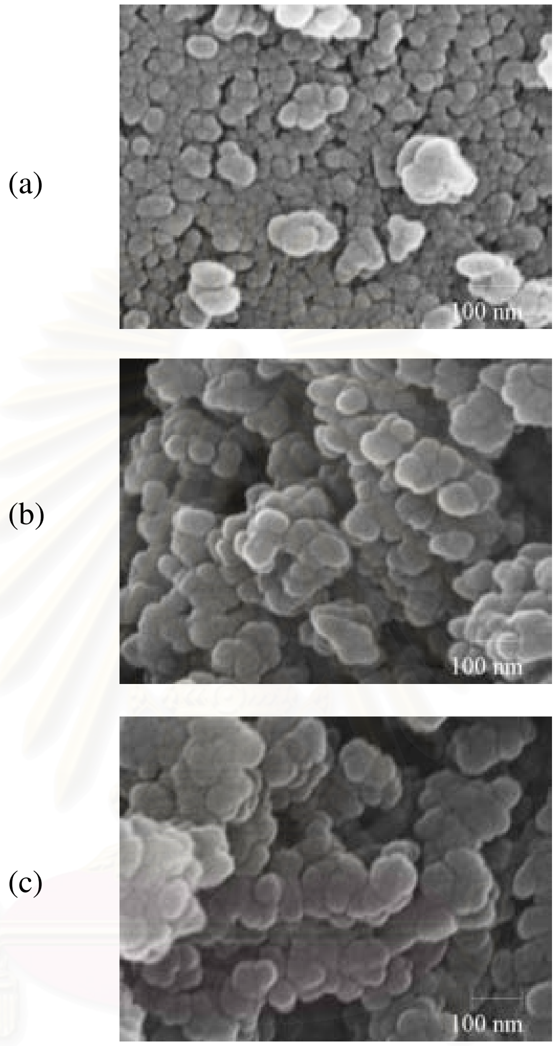


FIG. 4-26 Scanning Electro Microscope (SEM) of silica without admicelle adsorbed on the surface (a), compares to the silica adsorbent with mixed SDS/PODD (1:3 ratio) admicelles on the surface (b), and the silica adsorbent with PODD alone admicelles on the surface (c) (Magnification 80 K).

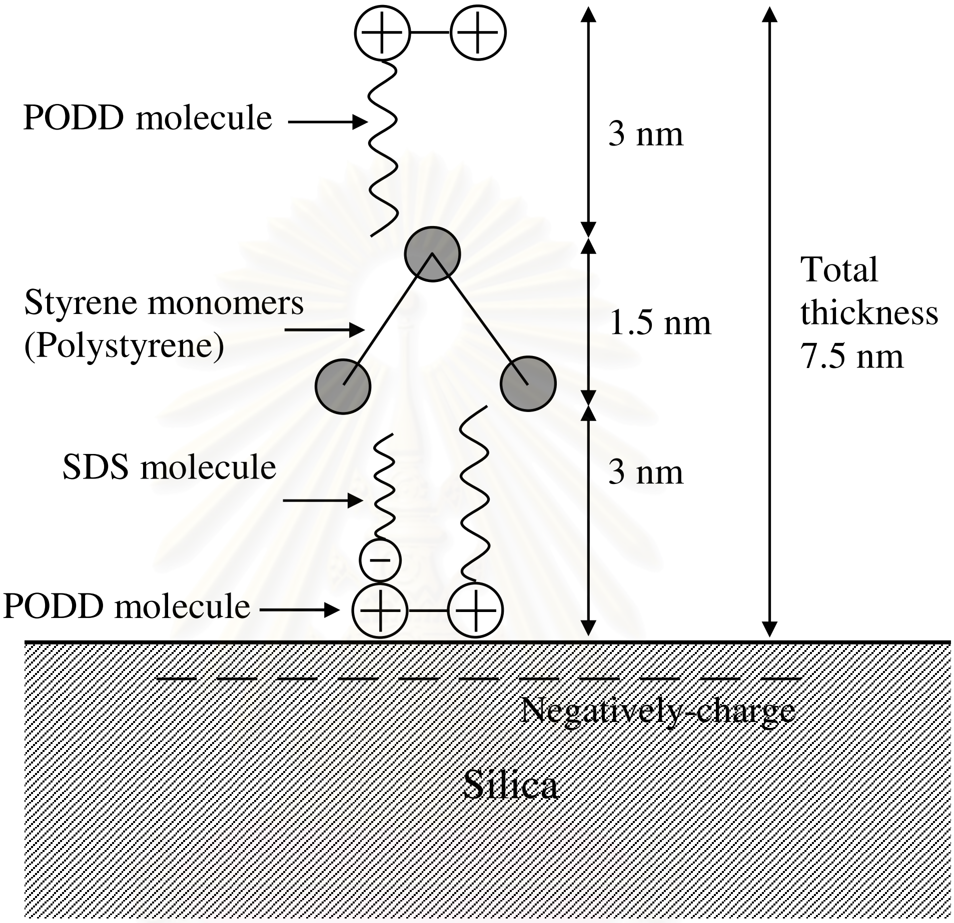
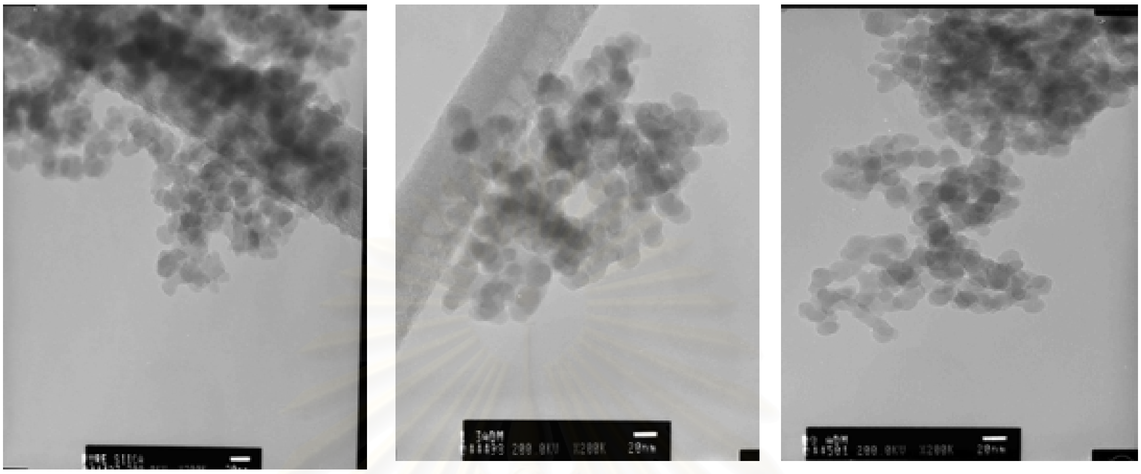


FIG. 4-27 Idealized arrangement and thickness of admicelle.

4.8.1 TEM (Transmission Electron Microscopy)

Figure 4-28 shows the particles of silica without admicelles adsorbed on the surface as compared to the particles of silica adsorbent with mixed SDS/PODD admicelles and PODD-alone admicelles adsorbed on the surface (Figure 4-28 (b) and Figure 4-28 (c), respectively). Since the magnification of the image is 200 K (200,000 times enlargement), the characteristic of the particles is hard to identify. Nonetheless, the size of the adsorbents with mixed SDS/PODD admicelles and PODD-alone admicelles are qualitative observed to be bigger than that of the particles of silica without admicelles. Future research should further explore these observations.



(a) (b) (c)

FIG. 4-28 Transmission Electro Microscope (TEM) of silica without admicelle adsorbed on the surface (a), compares to the silica adsorbent with mixed SDS/PODD (1:3 ratio) admicelles on the surface (b), and the silica adsorbent with PODD alone admicelles on the surface (c) (Magnification 200 K).

CHAPTER V

SUMMARY

The study of mixed anionic and cationic surfactants demonstrated synergism in many different experiments, such as shrinking the precipitation area of mixed surfactant, enhancing surfactant adsorption on particle surfaces and increasing the solubilization and the adsolubilization of organic solutes into mixed micelles and mixed admicelles. Mixed anionic and cationic surfactants adsorbed on surfaces can slow down the flow of organic solutes while passing through the adsorbent.

From this study, we found that mixed surfactants reach the CMC and form micelles at lower concentrations than single surfactant systems. Thus, when we apply mixed surfactant in the contaminated subsurface, we use less surfactant than single surfactant systems. The study also showed higher solubilization of organic solutes into mixed micelles than into the micelles of single surfactant systems. Using mixed surfactants for groundwater remediation thus can improve the economics, because less cleaning material is required.

The pump and treat method is suitable for high concentration of the contaminant in the subsurface. When the concentration of the contaminant is reduced, continuing this method is considered to be less economical. Some of the surfactant is left in the subsurface by adsorbing on the soil particles. The loss of surfactant causes more expense and affects to the environment. Even if most of the surfactants are degradable grade, but it takes time to degrade if surfactants are high concentration. In this case, the alternative method is chosen. The use of adsorbent is one of the methods. Mixed surfactant admicelles adsorbed on mineral oxide surfaces can hold more oil with longer time than single surfactant admicelles. Thus, the adsorbent can capture the contaminant and let the biodegradation process clean the oil. The adsorbent can be regenerated if the organic solute is captured until the adsorbent is saturated. The surfactant and the mineral oxide can be reused, while the captured organic solute is eliminated.

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BIOGRAPHY

Mrs. Aranya Fuangswasdi was born on October 16, 1957 in Si Sa Ket, Thailand. She graduated from Benchamarachalai School, Bangkok in 1976 and received Bachelor's Degree of Science (Geology) from Chulalongkorn University in 1981. She got married and has two children, a girl and a boy. She started her career as a geologist for the Department of Mineral Resources. After working for years, she went to Australia for her Master's Degree in Groundwater Management in 1990-1991. She continued her career as a hydrogeologist for the Ground Water Division, Department of Mineral Resources. In 1999, the Department was structurally reformed including the establishment of the Department of Groundwater Resources, under the Ministry of Natural Resources and Environment. She was supported from her family to further her study coping with the new role of the Department. She started her Philosophy of Doctoral Degree study in the International Postgraduate Programs in the Environmental Management, Inter-Department of Environmental Management, Chulalongkorn University, Bangkok, Thailand in May 2002. She finished her Philosophy of Doctoral Degree of Science in Environmental Management in April 2006.