CHAPTER III

Adsorption and Adsolubilization Using Polymerizable Surfactants onto Aluminum Oxide Surface

ABSTRACT

Recently, surfactant-based adsorption processes have been widely investigated for environmental application. One of the problems of using surfactant modified adsorbent is loss of surfactants from the adsorbent due to pH changes or dilution of surfactant concentration and desorption. For this study, a bilayer of anionic polymerizable surfactants (Hitenol BC 05 and BC 20) and non-polymerizable surfactant (Hitenol N 08) were adsorbed on the alumina. The results of adsorption studies showed that as the number of EO groups of the surfactants increased, the area per molecule increased and the maximum adsorption decreased. The lowest maximum adsorption onto alumina was obtained at the number of EO groups of 20 of Hitenol BC 20 corresponding to 0.08 mmole/g or 0.34 molecule/nm^2 while the highest level of adsorption was 0.30 mmole/g or 1.28 molecule/nm^2. This variation in adsorption was attributed to the increasing bulkiness of the head with number of EO groups. For adsolubilization capacity of organic solutes, increasing the number of EO groups of the surfactants decreased the adsolubilized styrene and increased the adsolubilized ethylcyclohexane. For the surfactant desorption study, the polymerization of polymerizable surfactants could enhanced the stability of surfactants adsorbed onto alumina surface and reduce desorption of the surfactants from alumina surface. These results provide the useful information of the surfactant systems for designing surface modification to enhance contaminant remediation and industrial scale applications.

Keywords: admicellar polymerization, adsolubilization, alumina, irradiation, polymerizable surfactants, polymerization

1. Introduction

Due to the limitations of pump and treat systems, recently, there have been many studied focused on surfactant – based processes. According to the applications, surfactant – based adsorption processes have been widely investigated for use in environmental application (West and Harwell, 1992; Sabatini et al., 2000). Although surfactant – based adsorption processes can be used in many application, there have been the problems that oppose the economics of the system. Surfactant loss is one of the problems that is typically well known, for example, precipitation, sorption, etc.(Rouse et al., 1993; Thakulsukanant et al., 1997; Sabatini et al., 2000; Gadelle et al., 2001). Particularly, the desorption is the phenomenon that the surfactants have been detached from adsorbent because of heating, difference pH of solution and dilution of surfactant concentration. Therefore, polymerizable surfactants are of interest for fixation of surfactants on the solid surface because polymerization of polymerizable surfactant brings about the strong linkage of surfactants coating on the solid surface. In consequence of layers of surfactants adsorbed onto solid oxide surface, they can be considered as a two – dimensional solvent, and organic solutes can partition into the adsorbed surfactants called adsolubilization. The adsolubilization can be used for many application, for instance, admicellar polymerization has been used to improve rubber physical properties. Moreover, admicellar chromatography is a separation process by inducing organic solutes partitioning into surfactant from aqueous phase including pollutant removal for water and soil remediation (Kitiyanan et al., 1996; Esumi et al., 2000; Pongprayoon et al., 2003).

The overall objectives of this study are to investigate adsorption of polymerizable surfactants onto positively charged aluminum oxide surface, to determine adsolubilization of organic solutes into admicelles, and to evaluate to the desorption potential of polymerized admicelles. The specific objectives of this study are to investigate the surfactant adsorption both polymerizable surfactants

and non-polymerizable surfactant, to evaluate the effect of polarity of organic solutes on the adsolubilization, and to evaluate the stability of surfactant adsorbed on the alumina after polymerization of the admicelles.

2. Background

Surfactants are **amphiphilic molecules** because they consist of polar or hydrophilic portion as head groups and non-polar or lipophilic portion as tail groups in the same molecule. They are able to assemble in many different forms of aggregates, depending on the concentration of surfactant in aqueous solution. At low concentration, surfactants called **monomers** act independently from the others. When the surfactant concentration increase until it exceeds the certain point, the surfactant monomers will aggregate to spherical aggregates called **micelles**. The concentration where the first micelle appears is called **the critical micelle concentration (CMC)**. When a solid phase is added to the surfactant solution, the surfactants will aggregate at the solid-liquid interface. At a high enough concentration, the adsorbed surfactant molecules interact on the solid surface and form micelle-like structures called **hemimicelles** and **admicelles**, depending on whether the aggregates are monolayer or bilayer (Rosen, 1989). The surfactant adsorption onto solid oxide surfaces such as alumina is a complex process. The adsorption isotherm, which experimented about the aqueous surfactant concentration and surfactant adsorption onto a solid surface at constant temperature, are used for identifying the adsorption (Kitiyanan, et al.,1996). Equation 1.1 can be used to calculate the equilibrium adsorption of the surfactant on the solid oxide surface. This equation is assumed that it neglects the adsorption of water or salt and the adsorption of the surfactant have no effect on solution density (Lopata, 1988).

$$\Gamma_i = \frac{(C_{i,b} - C_{i,a})V}{W_g} \tag{3.1}$$

where Γ_i is the adsorption density of surfactant i in mole/g, V is the volume of sample in liter, $C_{i,a}$ is

the concentration of surfactant at equilibrium in molar, $C_{i,b}$ is the concentration of surfactant at initial

in molar, and W_g is the weight of aluminum oxide in g. The adsorption isotherm of ionic surfactants on

oxide surfaces is typically an elongated 'S'-shaped curve that can be separated into four regions

(Somasudaran and Fuerstenau, 1966; Scamehorn, et al., 1982). Figure 3.1 shows these four regions

in the plot between the log of the adsorbed surfactant density versus the log of the equilibrium
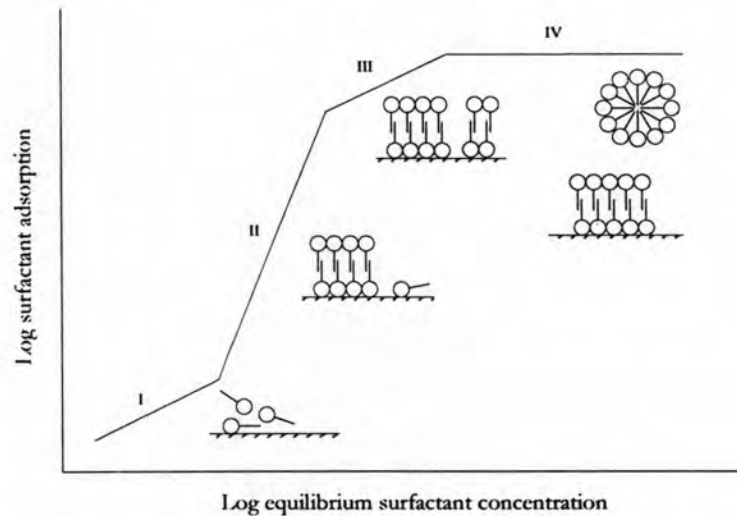
concentration of surfactant.

Figure 3.1 Schematic presentation of typical surfactant adsorption isotherm

Region I, as very low concentration region, is referred to as the Henry's law region because

surfactant monomers are infinitely diluted in the surface phase and, thus, the interaction between

molecules of surfactants is negligible. The slope in Region II is isolated by a sharply increased

relatively compared to the slope in region I because of the beginning of lateral interactions between

surfactant molecules. The transition point from region I to region II, representing the first formation of

adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) or the

hemimicelle concentration (HMC). Region III is the region that has the isotherm decreasing from the

slope in Region II because of the beginning of admicelle formation on lower energy surface patches

or the adsorption now must overcome electrostatic repulsion between closed ions and the similarly

charged solid surface. Region IV is the plateau region, that have almost constant surfactant

adsorption, while the surfactant concentration increase. The transition point from region III to region

IV, representing the first formation of micelles after the interface is saturated by admicelles,

corresponds to the critical micelle concentration(CMC) (Kitiyanan, et al., 1996; Charoensaeng, 2003).

Surface tension, or excess surface free energy, is equivalent to a force per unit length or a

Gibbs(free) energy per unit area. The surface tension is the parameter that indicates the interaction

forces between molecules in the surface region and neighbors. The magnitude of surface tension

depends on the cohesive energy density of molecules. The concentration of surfactant at the

interface may be calculated from surface or interfacial tension data by use of the appropriate Gibbs

equation as in equation 3.2 and 3.3(Rosen, 1989; Harwell, 2006).

For 1:1 ionic surfactant in the presence of a swamping amount of electrolyte containing a common

nonsurfactant ion,

$$\Gamma = -\frac{1}{2.303RT}\left(\frac{\partial \gamma}{\partial \log C_1}\right)_T \tag{3.2}$$

For 1:1 ionic surfactant in the absence of any other solutes,

$$\Gamma = -\frac{1}{4.606RT}\left(\frac{\partial \gamma}{\partial \log C_1}\right)_T \tag{3.3}$$

where γ is the interfacial tension in N/m, R is equal to 8.314 J mol^{-1} K^{-1}, T is equal to 298 K at 25°C,

and C_1 is surfactant concentration in molar. From the surface excess concentration, the area per

molecule at the interface a_1^s, in square angstroms is calculated from the equation 3.4,

$$a_1^s = \frac{10^{23}}{N\Gamma_1} \tag{3.4}$$

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

There are a number of parameters involving the adsorption of surfactants on solid surfaces

from aqueous solution, for example, the nature of the structural groups of the solid surface, the

molecular structure of surfactant adsorbed on the solid surfaces and the environment of the aqueous

solution such as equilibrium pH, temperature, and electrolyte concentration (Esumi et al., 1996). pH causes significantly changes in the adsorption of ionic surfactants onto charged solid surface (Harwell et al., 1985). As the pH of the aqueous solution is lowered, a solid surface will usually turn into more positive. Consequently, the adsorption of anionic surfactants increases, whereas the adsorption of cationic surfactants decreases. A rise in temperature usually causes an increase in the adsorption of nonionic surfactants containing a polyelectrolyte chain as the hydrophilic group, this has been consequently attributed to decrease solute-solvent interaction. Counter ions can influence the adsorbed surfactants because they reduce the electrostatic repulsion between the adsorbed ionic surfactant head groups. The higher the counter-ion concentration, the more easily admicelles are formed. The maximum surfactant adsorption also increases (Lopata, 1988; Charoensaeng, 2003).

The partition of organic solutes from aqueous solution will be soluble in the hydrophobic portion or the core, depending on whether they are adsorbed on micelles or admicelles. Adsolubilization is phenomenon that the organic solutes are adsorbed on admicelles (surfactant bilayer). Similarly, solubilization is phenomenon that the organic solutes are adsorbed on micelles. Figure 3.2 shows the phenomena of solubilization and adsolubilization.
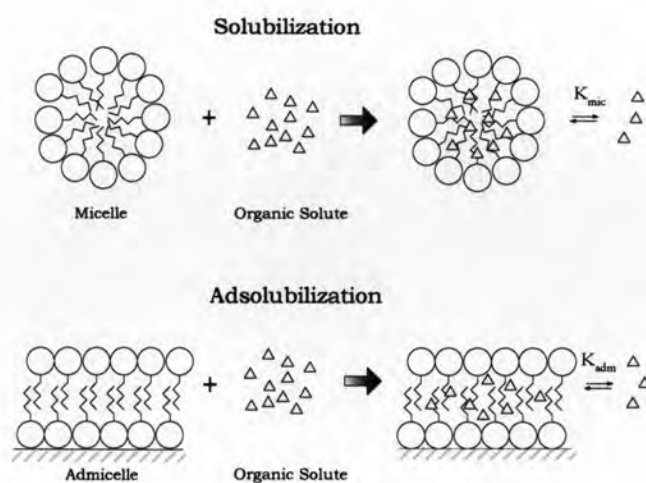

Figure 3.2 Phenomena of solubilization and adsolubilization

Figure 3.2 shows that the admicelle which has the bilayer structure is divided into three-regions similar to a micelle. The outer region is the most polar or ionic region because it is comprised of the surfactant head group. The inner region or the core region is non-polar region because it is comprised of the hydrocarbon chain of surfactant tail groups. The palisade region has intermediate polarity because it is the region between surfactant head groups and the core region (Nayyar, 1994; Dickson and O'Haver, 2002). The partition of various organic solutes into the admicelles can be described by admicellar partition coefficient as shown in equation 3.5,

$$K_{adm} = \frac{X_{adm}}{X_{aq}}$$

(3.5)

where X_{adm} is the mole fraction of organic solute in the admicelle phase, and X_{aq} is the mole fraction of organic solute in the aqueous phase. For this study, X_{adm} values are calculated as:

$$X_{adm} = \frac{(C_{i,S} - C_{f,S})}{(C_{i,S} - C_{f,S}) + (S_i - S_f)}$$

(3.6)

where X_{adm} is mole fraction of organic solute in admicelle, $C_{i,S}$ and $C_{f,S}$ are initial and final concentration of organic solute in molar, respectively, and S_i and S_f are initial and final concentration of surfactant in molar, respectively. X_{aq} is calculated from equation 3.7,

$$X_{aq} = \frac{C_{f,s}}{C_{f,s} + 55.55}$$

(3.7)

where 55.55 represent 1/molar volume of water.

The adsolubilization has been applied in very different areas such as pharmacy, cosmetic, soil remediation, wastewater treatment, ultra thin film formation. In addition, the adsolubilization has been used as the important phenomenon in many processes, for example, admicellar polymerization, and admicellar chromatography (Esumi et al., 1998; Merino et al., 2003).

One of the problems of using surfactant modified adsorbent is the loss of surfactant from the surface during application. A previous column study showed that surfactant loss occurred when the solution pH contacting with admicelles changed (Krajangpan, 2004). Heating, difference of pH, and

dilution of the surfactant make the equilibrium shift, and the surfactant will desorb from the adsorbent surface (Esumi, et al., 1993). Recently there have been many studies on polymerizable surfactant. Polymerizable surfactant is a surfactant that can be polymerized at the double bond in the molecule. Polymerization of the surfactant can enhance dispersion stability of the alumina with the polymerized film (Esumi, et al., 1989 and 1991; Berg and Claesson, 1994; Hirai et al., 2000). It reduces the desorption of the surfactant from the alumina surface.

The purposes of this study are to evaluate stability of the surfactant adsorbed on the alumina coated with polymerized film of polymerizable surfactant related with the desorption of the surfactant, to compare the surfactant adsorption and the organic solute adsolubilization capacity with and without polymerization of surfactant, and to examine the effect of polarity of organic solutes on the adsolubilization capacity with the goal to enhance the ability of surfactant modified adsorbent for environmental remediation.
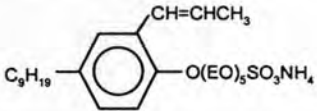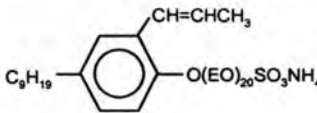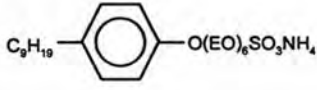
3.   Experiment Section

(i)Experiment Approach. The adsorption of surfactant and the adsolubilization of organic solutes were conducted in batch experiments at room temperature ($25 \pm 2\ ^\circ C$), constant pH solution in the range of 7 ± 0.5, and electrolyte concentration of 0.001 M NaCl. The adsolubilization of organic solutes, styrene and ethylcyclohexane were conducted to evaluate the adsolubilization capacity of organic solutes with different degree of polarity in admicelles.

(ii) Materials. Poly(oxy-1,2-ethanediyl), α-sulfo-ω-[4-nonyl-2-(1-propenyl)phenoxy]-, branched ammonium salts or Hitenol BC 05 and Hitenol 20, which have the number of ethylene oxide (EO) group of 5 and 20, respectively, were used in this study as an anionic polymerizable surfactant and Poly(oxy-1,2-ethanediyl), α-sulfo-ω-[4-nonyl-phenoxy]-, branched ammonium salts or Hitenol N 08, which have the number of ethylene oxide (EO) group of 6, was used in this study as an non-
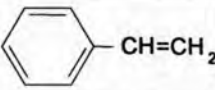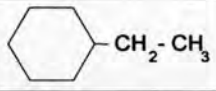
polymerizable surfactant. These surfactants were obtained from Montello, Inc. The properties

surfactants are shown in Table 3.1. HLB is hydrophilic and lipophilic balance that can indicate

hydrophilicity of the surfactants (Sabatini, 2006).

Table 3.1 The properties of surfactants used in this study

Surfactant	Type	MW	% active	Molecular structure	HLB
Hitenol BC 05	Anionic	580	97	C_9H_{19}—⟨benzene ring⟩—$CH=CHCH_3$, $O(EO)_5SO_3NH_4$	40.10
Hitenol BC 20	Anionic	1240	97	C_9H_{19}—⟨benzene ring⟩—$CH=CHCH_3$, $O(EO)_{20}SO_3NH_4$	45.05
Hitenol N 08	Anionic	581	96.33	C_9H_{19}—⟨benzene ring⟩—$O(EO)_8SO_3NH_4$	41.86

Styrene and ethylcyclohexane were selected as a higher and lower polar organic solutes,

respectively. Styrene and ethylcyclohexane (99% purity) were purchased from Arcos chemical

company. The properties of organic solutes are shown in Table 3.2.

Table 3.2 Properties of organic solutes

Organic solute	MW [b]	Molecular formula		Solubility in water(Molar)	Density (g/mL)25 °C	K_{ow}	Dipole Moment
		Formula	Structure				
Styrene [a]	104.15	C_8H_8	⟨benzene ring⟩—$CH=CH_2$	0.0027	0.909	2.95	0.13
Ethylcyclohexane [c]	112.21	C_8H_{16}	⟨cyclohexane ring⟩—CH_2-CH_3	0.0012	0.788	4.40 [c]	0.00

[a] data from http://www.risk.lsd/ornl.gov. [b] data from http://www.chemfinder.com. [c] data from (Gustafson et al., 1997)

Aluminum oxide or alumina (Al_2O_3), mesh size 150, was purchased from Aldrich chemical company

and used as received. The point of zero charge (PZC) of aluminum oxide is 9.1(Sun and Jaffe, 1996).

Thus, water suspensions of alumina were weakly acidic (pH of 6.75). The surface area was

determined to be139.36 m^2/g by N$_2$ BET adsorption method, whereas the specific surface area from manufacturer product is 155 m^2/g. All chemicals which were used as received are ACS analytical reagent grade. All solutions were made with double-distilled water. Plastic and glassware were rinsed well with double-distilled water three times prior to use.

(iii) Experimental Methods. This study was divided into four experimental parts. All experiments were conducted in batch experiments at room temperature (25 $\pm$ 2°C), constant pH solution in the range of 7 $\pm$ 0.5, and electrolyte concentration of 0.001 M NaCl.

a) Surfactant Adsorption Study. The surfactant adsorption isotherm onto positively charge surface of aluminum oxide (Al$_3$O$_2$) was studied. Different amounts of alumina were added into several vials containing 40mL of surfactant solution. All solutions were shaken for at least 48 hours until they reached equilibrium. Solution pH was periodically measured and adjusted to 7 $\pm$ 0.5. After being equilibrated, the solution was centrifuged to remove the alumina. The concentration of surfactants in supernatant was then determined by High Performance Liquid Chromatography (HPLC 1100, Agilent) with UV detector without column.

b) Surfactant Polymerization Study. The surfactant solution with alumina at equilibrium adsorption concentration was added with 0.5 g. of sodium persulfate as initiator. After purging with nitrogen gas to remove dissolved oxygen, the suspension was irradiated with a UV lamp (9815 series, Cole - Palmer Instrument Company with UV lamp 2✕15 watts) placed about 10 cm. away from the sample for 18 hours. The suspension was shaken during the polymerization.

c) Adsolubilization Study. The adsorption isotherm was used for determining the appropriate concentration in which the maximum surfactant coverage on the solid surface occurs without the presence of micelles in the bulk solution. In general, this point was slightly below the CMC of the

surfactants. This surfactant concentration and the amount of alumina corresponding to this surfactant concentration were used for the next adsolubilization experiment. Adsolubilization experiment was performed after polymerization by varying organic solute concentration with the appropriate surfactant concentration and the amount of alumina from the surfactant adsorption study. The solution was shaken for 48 hours and then centrifuged to remove alumina. The surfactant concentration and the organic solute concentration in aqueous solution were analyzed by High Performance Liquid Chromatography (HPLC 1100, Agilent) with UV detector without column and Gas Chromatography (GC 6890N, Agilent) with FID detector, respectively.

d) Surfactant Desorption Study. The surfactant desorption study was studied to examine the amount of surfactants that desorb from alumina surface after washing process and the effects of pH. It was conducted after surfactant polymerization. The prepared adsorbent, alumina coated with polymerized film of surfactant was washed by deionized water about 10 times in batch experiment at room temperature ($25\pm2^\circ$C) to make sure that the surfactant monomers or micelles have not remained on the adsorbent. After washing process, the adsorbent in deionized water was shaken at least 48 hours that is the same as adsoption experiment. After that, the surfactant concentration in the solution before and after shaking was observed for desorption of surfactants from alumina surface by UV/Visible spectrophotometer (Helios-Alpha, Thermo Electron Corporation).

(iv) Analytical Methods. Surfactant concentration was analyzed by High Performance Liquid Chromatography (HPLC 1100, Agilent) with UV detector without column. Gas chromatography(GC 6890N, Agilent), with FID detector was used for analyzing the concentration of organic solutes, styrene and ethylcyclohexane. The surfactant concentration in desorption study was analyzed by UV/Visible spectrophotometer (Helios-Alpha, Thermo electron corporation).

4.   Results and Discussion

(i) Surfactant Adsorption Study. The adsorption of anionic polymerizable surfacntants and non-polymerizable surfactant onto positively charged aluminum oxide surface was studied in batch experiments at room temperature ($25 \pm 2°C$), constant pH solution in the range of 7 ± 0.5, and at an electrolyte concentration of 0.001 M NaCl. The surface tension is the parameter that indicates the interaction forces between molecules in the surface region and neighbors. It was used to calculate the critical micelle concentration (CMC) from plot between surface tension versus surfactant concentration as shown in Figure 3.3.
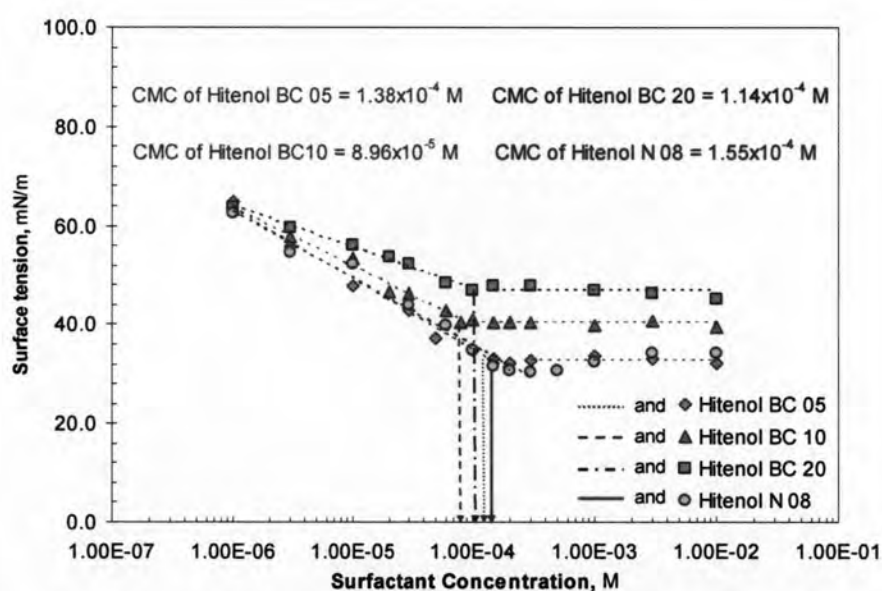
Figure 3.3 The interfacial surface tension of Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08 at electrolyte concentration of 0.001 M NaCl, equilibrium pH of 7 ± 0.5 and temperature of 25 ± 2 °C

From Figure 3.3, the results show that the surface tension decreases with increasing surfactant concentration. The break points were estimated as critical micelle concentration (CMC) at which minimum surface tension occurs as shown in Table 3.3. From the slope of the surface tension, the surfactant adsorption (Γ) and area per molecule are evaluated and are also shown in Table 3.3.

Table 3.3 Experimentally determined CMCs from surface tension, the minimum surface tension, surfactant adsorption, and area per molecule for Hitenol BC 05, BC 10, BC 20 and Hitenol N 08

Type of surfactants	CMC from surface tension (M)	Slope	r^2	Min. surface tension (mN/m)	stdev	Surfactant Adsorption (Γ) (mole/1000m^2)	Area per molecule (A^2/molecule)
Hitenol BC 05	1.38x10-4	-6.18	0.99	32.88	± 0.66	1.23x10-3	135.29
Hitenol BC 10^d	8.96x10-5	-5.20	0.99	40.32	± 0.54	1.05x10-3	158.34
Hitenol BC 20	1.14x10-4	-3.63	0.99	46.78	± 1.13	7.22x10-4	230.21
Hitenol N 08	1.55x10-4	-5.88	0.98	32.88	± 1.75	1.33x10-3	124.32

^{d} data for Hitenol BC 10 from Emma Asnachinda

The results from surface tension showed that increasing the number of EO group cause of larger area per molecule, lower surfactant adsorption and higher minimum surface tension. It was also found that there had been no trend of the CMCs of the surfactants when the number of EO group increased. Therefore, these CMCs were used to compare with the CMCs from the adsorption isotherm.

The surfactant adsorption isotherm was plotted between the log of the adsorbed surfactant density versus the log of the equilibrium concentration of surfactant. The maximum adsorption was evaluated as the mean value at the plateau region of the surfactant adsorption isotherm. Figure 3.4 is a surfactant adsorption isotherm of Hitenol BC 05, BC 10, BC 20 and Hitenol N 08.
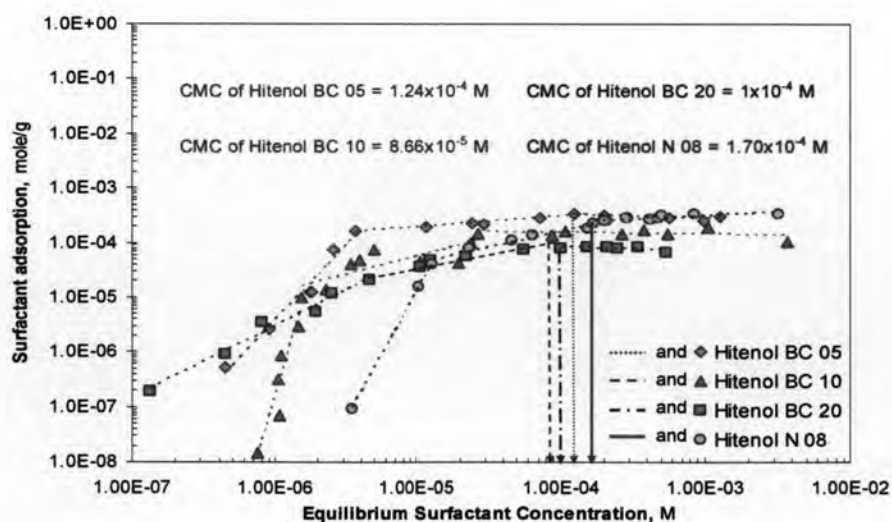
Figure 3.4 The adsorption isotherm of Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08 onto alumina at electrolyte concentration of 0.001 M NaCl, equilibrium pH of 7 ± 0.5 and temperature of 25 ± 2 °C

The results show that the adsorptions of these surfactants increase with increasing

equilibrium concentration. The maximum adsorptions of these surfactants are shown in Table 3.4.

Table 3.4 Experimentally determined maximum adsorption, molecule per area, and CMCs from adsorption isotherm for Hitenol BC 05, BC 10, BC 20 and Hitenol N 08

Type of surfactants	CMC from adsorption isotherm (M)	Maximum adsorption (mmole/g)	Stdev	Molecule per area (molecule/nm^2)	Area per molecule (A^2/molecule)
Hitenol BC 05	1.24E-04	0.30	± 0.03	1.28	77.95
Hitenol BC 10[d]	8.66E-05	0.15	± 0.03	0.64	155.37
Hitenol BC 20	1.00E-04	0.08	± 0.01	0.34	298.33
Hitenol N 08	1.70E-04	0.28	± 0.03	1.22	81.80

[d] data for Hitenol BC 10 from Emma Asnachinda

From Table 3.4, the CMCs from the adsorption isotherms were found to be similar to the

CMCs from the surface tension. The results would be expected that when the number of EO group

increased, the CMCs of the surfactants should increase. In this case, it was found that there had

been no trend of the CMCs of the surfactants when the number of EO group increased and these

CMCs had small differences between them. Therefore, it could infer that a rise of the number of EO

group could not significantly change the CMCs of the surfactants. Hitenol BC 05, BC 10, BC 20, and

N 08 had approximately the maximum adsorption of 0.30, 0.15, 0.08, and 0.28 mmole/g,

respectively. Hitenol BC 20 had the lowest maximum adsorption that corroborated the highest area

per molecule which is consistent with results from surface tension data. This could be attributed to a

more bulky head for 20 EO groups compared with the others. In addition, because Hitenol BC 05

and N 08 have 5 EO groups and 6 EO groups, respectively, the maximum adsorption and the area

per molecule of Hitenol BC 05 were similar to that of Hitenol N 08 which is consistent with the number

of EO groups. It can be concluded that increasing the number of EO group cause of increasing the

area per molecule, and decreasing the maximum adsorption of the surfactants.

From the maximum adsorption and specific area of alumina, the coverage on alumina of

Hitenol BC 05, BC 10, BC 20, and N 08 were 1.3, 0.6, 0.4, and 1.2 molecule/nm^2 or 78, 155, 298, and

81 Å^2/molecule, respectively. These values could be compared to those for the area per molecule at surface saturation of surfactants at the water-air interface. The area/molecule of Hitenol BC 05, BC 10, BC 20, and N 08 were estimated from the slope of the surface tension to be 135, 158, 230, and 124 Å^2, respectively (see Table 3.3). If the admicelles were present as complete bilayer coverage, the area/molecule of Hitenol BC 05, BC 10, BC 20, and N 08 should be 68, 79, 115, and 62 Å^2, respectively. It could be concluded that the molecule of these surfactants is too large to adsorb in the very narrow pores of this alumina (69.70 Å by N_2 BET adsorption method), thus the observed area per molecule on the alumina surface is greater than the area per molecule estimated for complete bilayer coverage. It is believed that the aggregation of these surfactants on the alumina surface is most likely in the form of a local bilayer (admicelles) but that all the BET surface area is not accessible to these surfactants (Kitiyanan et al., 1996).

(ii) Adsolubilization study. The adsolubilization isotherms of styrene and ethylcyclohexane by Hitenol BC 05, BC 10, BC 20 and Hitenol N 08 at electrolyte concentration of 0.001 M NaCl, equilibrium pH of 7 $\pm$ 0.5, and temperature of 25$\pm$2°C were shown in Figure 3.5 and 3.8, respectively. Moreover, the number of EO groups and organic solute admicellar partitioning coefficient (K_{adm}) which indicated the organic solute adsolubilization capacity could be concluded in Table 3.5. The adsolubilization experiments were carried out with the surfactant concentration at right below its CMC in order to control the equilibrium concentration in the supernatant not exceed the CMCs to make sure that there has been no micelle in the bulk solution. This could be tested by adding pinacyanol chloride dye to the solution of water and alumina. When pinacyanol was added to the supernatant of surfactant concentration right below CMC and alumina, the supernatant became red and alumina became blue which indicated that the supernatant had no micelle aggregate. When pinacyanol was added to the supernatant of surfactant concentration above CMC and alumina, the supernatant turn into blue

which indicated that it had existing of micelles. However, the blue color also occurred within

admicelles on the equilibrated alumina surface. These facts confirmed that the formation of

admicelles on alumina surface and exclude micelles in the supernatant in bulk solution (Nunn et al.,

1982; Wu et al., 1989; Thakulsukanant et al., 1997).

Styrene is higher polar organic solute, which is expected to partition into the palisade

region. Ethylcyclohexane is lower polar organic solute, which is expected to partition into the core

region.

Table 3.5 The number of EO groups, styrene and ethylcyclohexane adsolubilization that consist of the orgaic solute
admicellar partitioning coefficient (K_{adm}) and log K_{adm}

| Type of surfactants	Number of EO groups	Styrene adsolubilization			Ethylcyclohexane adsolubilization		
		$K_{adm}(10^5)$	r^2	log K_{adm}	$K_{adm}(10^5)$	r^2	log K_{adm}
Hitenol BC 05	5	0.188	0.84	4.27	0.340	0.91	4.53
Hitenol BC 10[d]	10	0.096	0.67	3.98	2.340	0.82	5.37
Hitenol BC 20	20	0.087	0.94	3.94	2.840	0.90	5.45
Hitenol N 08	6	0.222	0.71	4.35	0.410	0.75	4.61

[d] data for Hitenol BC 10 from Emma Asnachinda

a) Styrene. The adsolubilization isotherms of styrene by Hitenol BC 05, BC 10, BC 20 and

Hitenol N 08 are shown in Figure 3.5. The results show that the amount of adsolubilized styrene

increased with increasing equilibrium styrene concentration for all adsolubilization isotherms. As

expected, the styrene adsolubilization attains a maximum that is the styrene concentration reached

the water solubility. Figure 3.6 shows the styrene admicellar partitioning coefficient (K_{adm}) of Hitenol

BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08 and these K_{adm} values were summarized in

Table 3.5. The results showed that as the number of EO group increased, the styrene admicellar

partitioning coefficients slightly decreased. This is consistent with solubilization results in previous

research (Tan and O'Haver, 2004; Tamura et al., 2001). The results are counterintuitive, and that

more research is necessary to clearly understand the trends. However, one possible explanation

could be that these surfactants are anionic surfactants, thus, EO group has less degree of

hydrophilicity as compared with head group (sulfonate group). Therefore, increasing the number of EO group caused of less polar in palisade region and resulted in a reduction of the adsolubilized styrene.
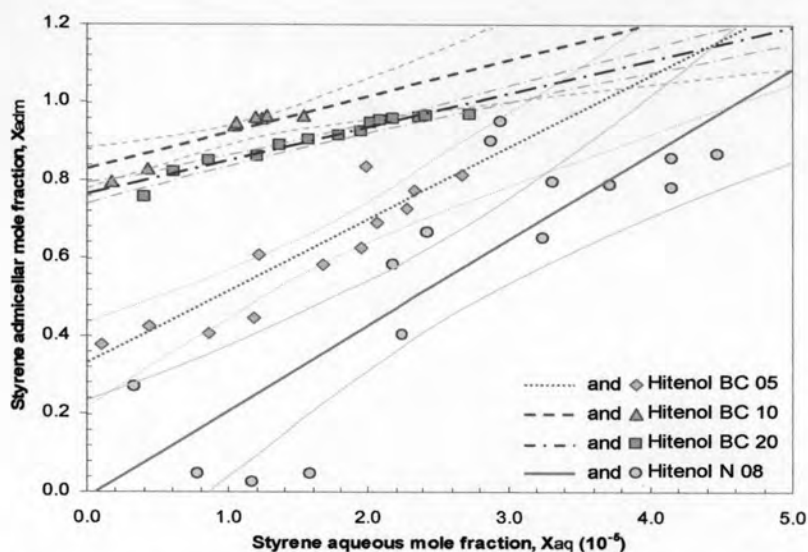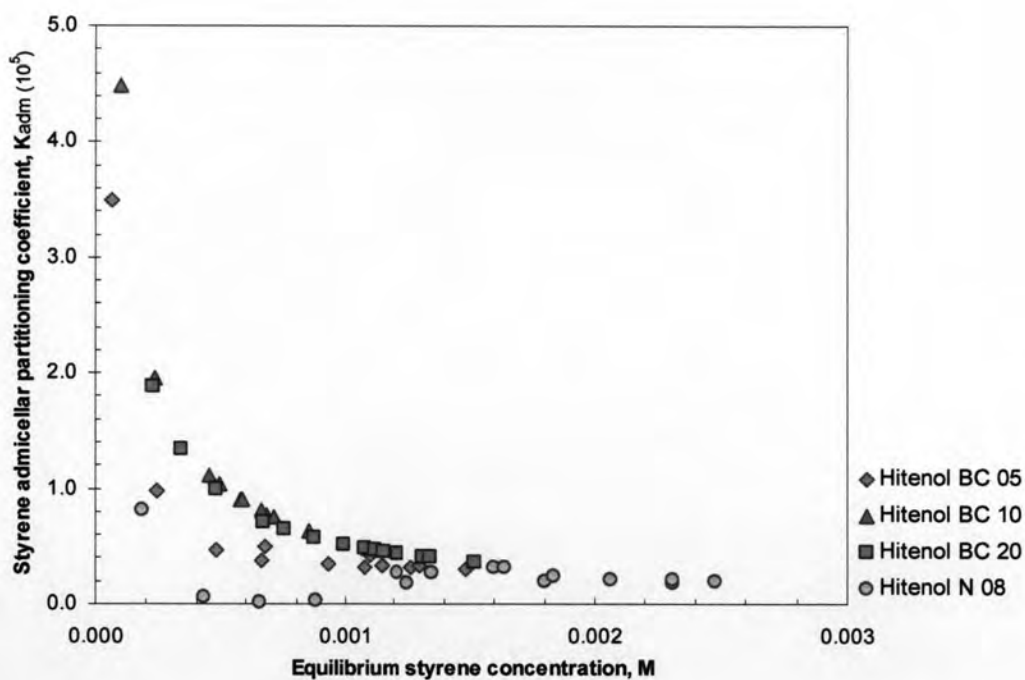

Figure 3.5 Adsolubilization of styrene by Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08 with 95% confidence intervals at electrolyte concentration of 0.001 M NaCl, equilibrium pH of 7 ± 0.5 and temperature of $25 \pm 2^{\circ}C$
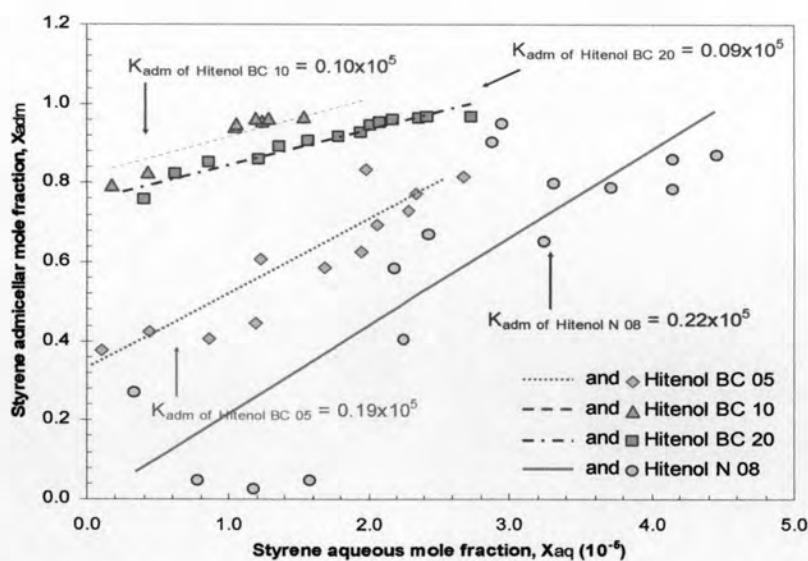
Figure 3.6 The styrene admicellar partitioning coefficient (K_{adm}), the slope from adsolubilization of styrene by Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08 at electrolyte concentration of 0.001 M NaCl, equilibrium pH of 7 ± 0.5 and temperature of $25 \pm 2^{\circ}C$

In order to achieve insight into the position of adsolubilization of styrene in the surfactants admicelles, the X_{adm}/X_{aq} or K_{adm} of styrene calculated from equation 3.5, were plotted against equilibrium styrene concentrations as shown in Figure 3.7. The K_{adm} gradually decreases with increasing equilibrium styrene concentration agreed with that the polar molecule as styrene is adsolubilzed into the palisade layer of the surfactant admicelles (Nayyar et al., 1994; Esumi et al., 2001; Dickson and O'Haver, 2002; Charoensaeng, 2003; Fuangswasdi et al., 2006b). However, there have been studies on the adsolubilization of styrene by a cationic surfactant bilayer onto precipitated silica. They found that styrene was adsolubilized in the both the core and the palisade region of the admicelles because the styrene adsolubilization constant is unchanged with increasing equilibrium styrene concentration in the aqueous phase (Kitiyanan, 1996; Tan and O'Haver, 2004).
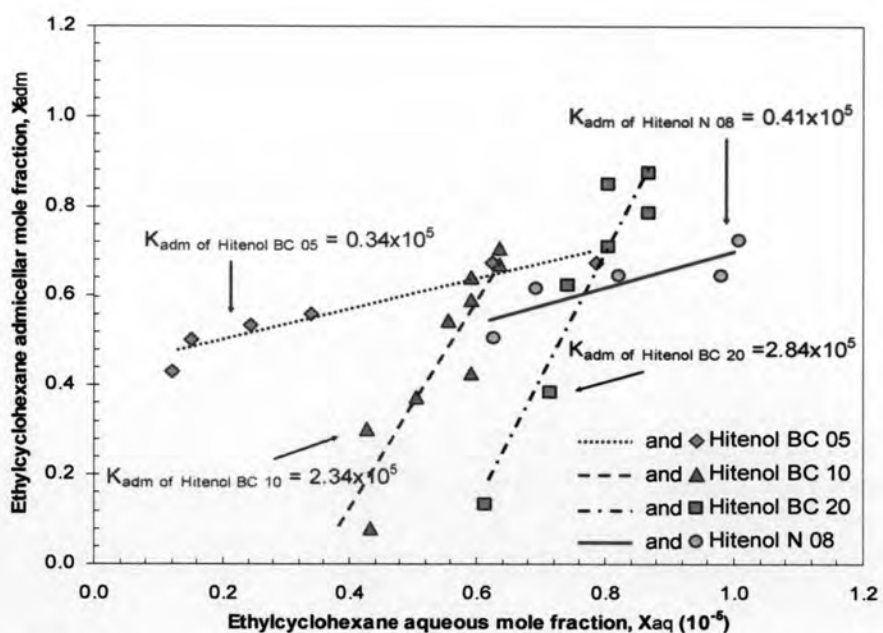

Figure 3.7 Plotted X_{adm}/X_{aq} of styrene versus styrene concentration at equilibrium for Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08

b) Ethylcyclohexane. The adsolubilization isotherms of ethylcyclohexane by Hitenol BC 05, BC 10, BC 20 and Hitenol N 08 are shown in Figure 3.8. The results show that the amount of adsolubilzed ethylcyclohexane increased with increasing equilibrium ethylcyclohexane concentration for all adsolubilization isotherms. The ethylcyclohexane adsolubilization also attains a maximum that is the ethylcylcohexane concentration reached the water solubility as expected like styrene. From the Figure 3.9, the ethylcyclohexane admicellar partitioning coefficients were calculated and summarized in Table 3.5. Due to the lower polarity of ethylcyclohexane, the adsolubilization capacity should be reverse compared with styrene adsolubilization capacity. It meant that as the number of EO group increased, the ethylcyclohexane admicellar partitioning coefficients gradually increased. Figure 3.10 shows the X_{adm}/X_{aq} or K_{adm} of ethylcyclohexane versus equilibrium ethylcyclohexane concentrations in order to indicate the locus of adsolubilization of ethylcyclohexane. For Hitenol BC 05 and N 08, the K_{adm} gradually decreases with increasing equilibrium ethylcyclohexane concentration, indicating that ethylcyclohexane partition into the palisade region. On the contrary, the K_{adm} steadily increases with increasing equilibrium ethylcyclohexane concentration for Hitenol BC 10 and BC 20 that shows ethylcyclohexane partitions into the core of admicelles. They partition differently into admicelles because of the effect of the number of EO group and the short chain length. Since EO groups acted as hydrophilic portion, Hitenol BC 10 and BC 20 have more EO group, and should have the higher hydrophilic region than Hitenol BC 05 and N 08. Moreover, ethylcyclohexane as lower polar molecule should partition into the core of the admicelles or hydrophobic region. Because of the short chain length and less EO number of Hitenol BC 05 and N 08, ethylcyclohexane should partition into palisade layer (spaces filling organic solutes of core region is not enough).
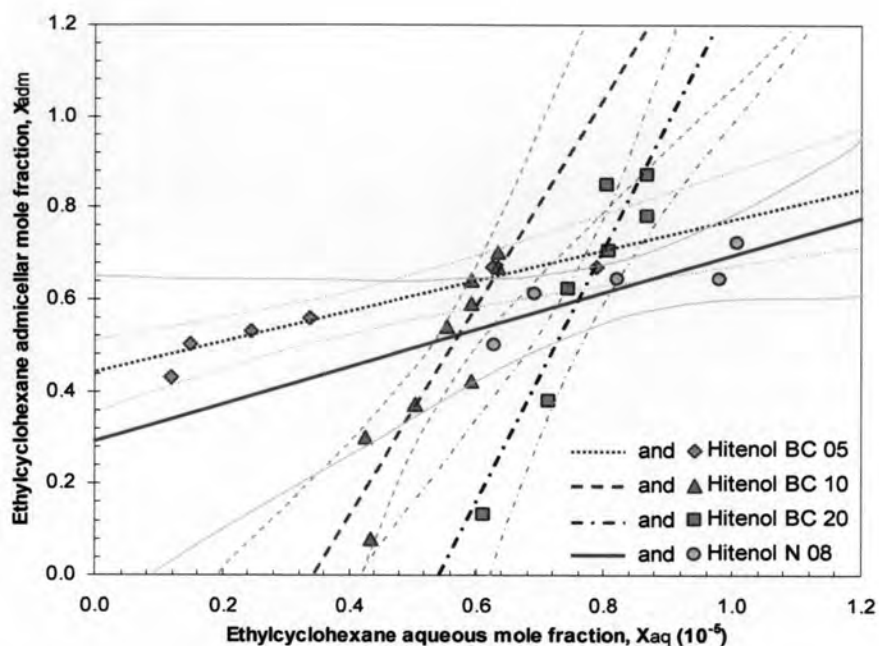
Figure 3.8 Adsolubilization of Ethylcyclohexane by Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08 with 95% confidence intervals at electrolyte concentration of 0.001 M NaCl, equilibrium pH of 7 ± 0.5 and temperature of $25 \pm 2\,^\circ$C


Figure 3.9 The ethylcyclohexane admicellar partitioning coefficient (K_{adm}), the slope from adsolubilization of ethylcyclohexane by Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08 at electrolyte concentration of 0.001 M NaCl, equilibrium pH of 7 ± 0.5 and temperature of $25 \pm 2\,^\circ$C
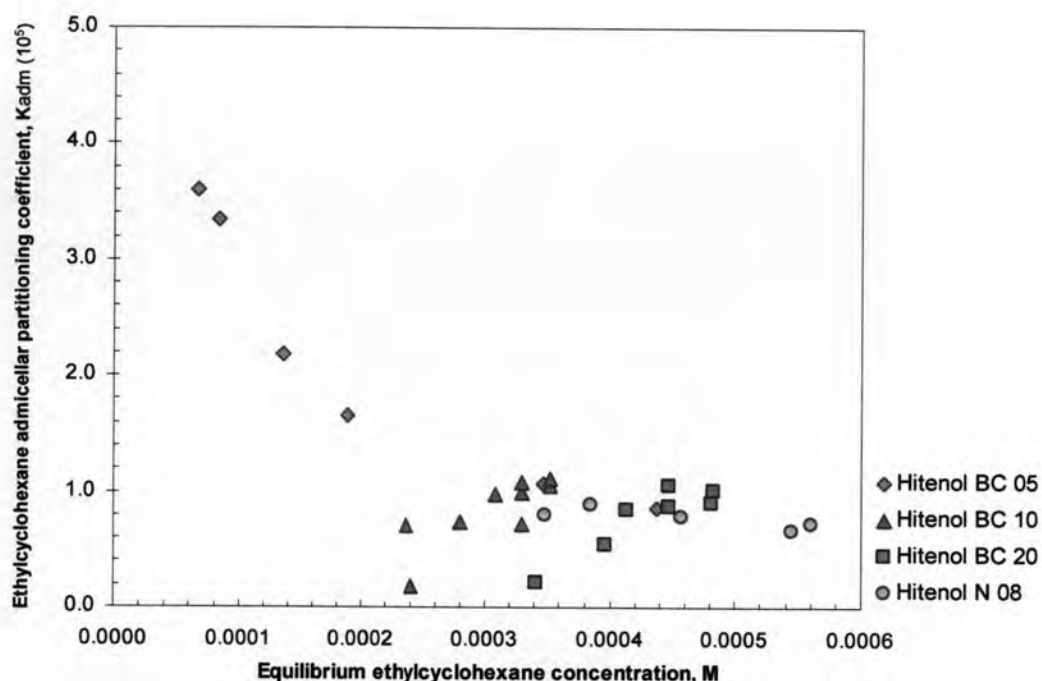
Figure 3.10 Plotted Xadm/Xaq of ethycyclohexane versus ethylcyclohexane concentration at equilibrium for Hitenol BC 05, Hitenol BC 10, Hitenol BC 20, and Hitenol N 08

(iii) Surfactant Polymerization and Surfactant Desorption Studies. Polymerization of the

polymerizable surfactants was confirmed by FTIR and UV spectrum. Figure 3.11 shows the example

of infared spectra of alumina coated with surfactants before and after polymerization and alumina

without surfactant. The results showed that the spectra of surfactants coated alumina both before

and after polymerization were different from the spectra of alumina. Due to polymerization, spectra in

the range of 1550-2600 nm before and after polymerization were similar, but in the range of 1000-

1550 nm the spectra of alumina with surfactant before polymerization was different from the spectra

of alumina with surfactant after polymerization. It was confirmed that the polymerization occurred.

For UV spectra at the wavelength of 240-250 nm, due to the double bond conjugated to the

benzyl group, the response was present before polymerization, but absent after the polymerization

(Berg and Claesson, 1994).
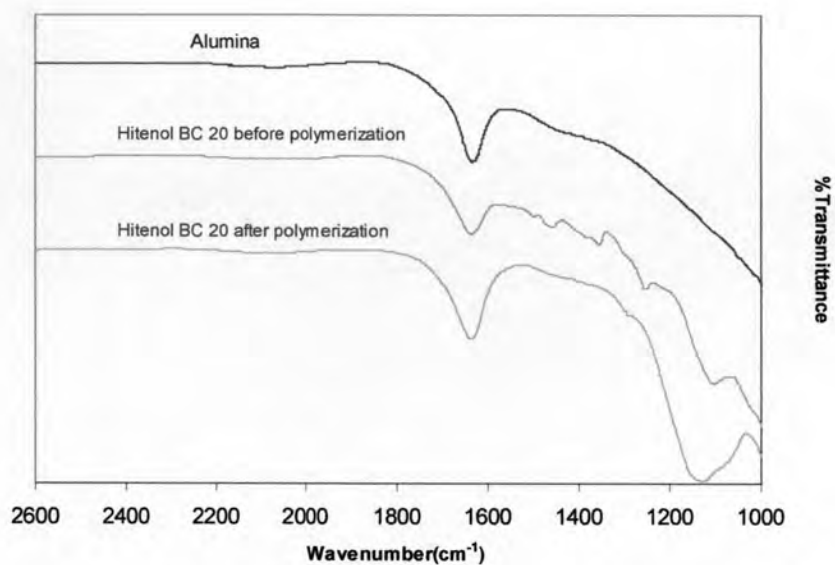
Figure 3.11 The FTIR spectra between 1000 and 2600 cm^{-1} of alumina, Hitenol BC 20 before polymerization, and Hitenol BC 20 after polymerization

For desorption study, the surfactant concentrations for each surfactant were chosen in three concentrations as monolayer, bilayer below CMC, and bilayer above CMC. The polymerized surfactants, the non-polymerized surfactants and the surfactants remaining after washing process were expected that they remained in bulk solution after desorbing but the non-polymerized surfactants and the surfactants remaining after washing process should existed at low concentration. The results were found that the response or peak area from UV/Visible spectrophotometer of the solution after irradiation increased as compared to the response before irradiation. However, the trend of increasing response was not observed. Thus, the calibration curve cannot be made and the related peak area was used to compare the desorption potential of the surfactants from alumina surfaces. Figure 3.12 and Table 3.6 showed that the desorption of Hitenol N 08 both with and without irradiation were more than that of the other surfactants because Hitenol N 08 was not polymerizable surfactant. Thus, it could not be fixed strongly on the alumina surface. Furthermore, Figure 3.12 and Table 3.6 also showed that the surfactants adsorbed in the bilayer both below and

above CMC could desorb easier than the surfactants adsorbed in the monolayer. This attributes to the electrostatic attraction in the monolayer, which is stronger than hydrophobic interaction in the bilayer. It can indicate that desorption begins from the bilayer and the monolayer later as expected that the desorption of the monolayer is very slow (Berg and Claesson, 1994).

From both surfactant polymerization study and surfactant desorption study, the response in UV spectra of non-polymerizable surfactant disappeared after polymerization, but it still desorbed from alumina surface. Therefore, it could be noted that the double bonds in benzene ring were broken, whereas the polymerization did not occur for the non-polymerizable surfactant.

5.   Conclusions

Surfactant-modification adsorbent appeared to be effective for the applications related to removal of organic pollutants and toxic substances from the environment. Polymerization of polymerizable surfactants can improve surfactant-modification adsorbent property. Due to the economic of the systems, polymerization can enhance the stability of the bilayer of the surfactants. Therefore, the surfactants can be fixed strongly onto the solid surface, so that the possible desorption of the surfactant molecule from the surface should be impeded. Furthermore, the polymerization can enhance the dispersion stability that is given the ready availability of the adsorbents for the industrial scale applications.

Table 3.6 The desorption of Hitenol BC 05, Hitenol BC 20, and Hitenol N 08 with and without irradiaiton

Type of surfactants	Monolayer	Bilayer (below CMC)	Bilayer (above CMC)
Hitenol BC 05	0.008	0.020	0.037
Hitenol BC 20	0.000	0.004	0.003
Hitenol N 08 (w/o irradiation)	0.008	0.038	0.069
Hitenol N 08 (irradiation)	0.000	0.027	0.059
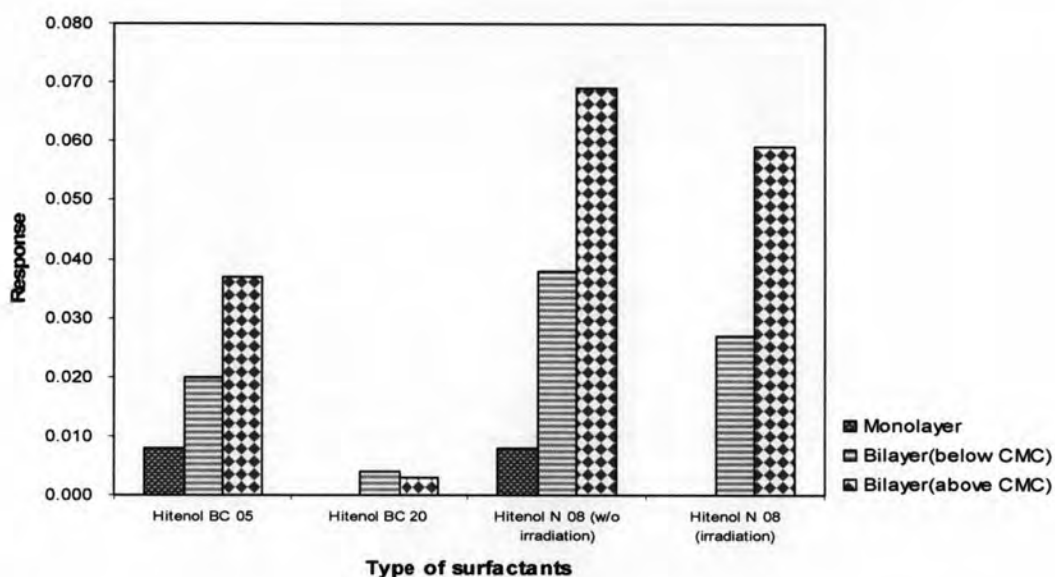
Figure 3.12 The desorption of Hitenol BC 05, Hitenol BC 20, and Hitenol N 08 with and without irradiation

ACKNOWLEDGEMENT

References:

1. Berg, J. M., Claesson, P. M. (1994). Forces between Surfaces Coated with a Polymerizable Surfactant before and after Polymerization. J. Colloid and Interf. Sci., 163, 289.

2. Charoensaeng, A. (2003). Adsorption of Mixed Anionic and Cationic Surfactant System onto Alumina. Master Thesis, Graduate School, Chulalongkorn University.

3. Dickson, J., and O'Haver, J. (2002). Adsolubilization of Naphthalene and Naphthol in CTAB Admicelles. Langmuir, 18, 9171.

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

5. Esumi, K., Maedomari, N., and Torigoe, K. (2001). Adsolubilization of 2-Naphthol by Binary Mixtures of Cationic and Nonionic Surfactants on Silica. Langmuir, 17, 7350.

6. Esumi, K., Matoba, M., and Yamanaka, Y. (1996). Characterization of Adsorption of Quaternary Ammonium Cationic Surfactants and Their Adsolubilization Behaviors on Siica. Langmuir, 12, 2130.

7. Esumi, K., Nakao, T., and Ito, S. (1993). Fixation of Polymerizable Surfactant on Alumina by UV Irradiation. J. Colloid and Interf. Sci., 156, 256.

8. Esumi, K., Toyoda, H., Goino, M., Suhara, T., and Fukui, H. (1998). Adsorption of Sodium Dodecyl Sulfate and 2-Naphthol Adsolubilization on Titanium Dioxide with Quaternary Ammonium Groups. Langmiur, 14, 199.

9. Esumi, K., Watanabe, N., and Meguro, K. (1989). Polymerization of Surfactant Bilayer on Alumina Using a Polymerizable Surfactant. Langmuir, 5, 1420.

10. Esumi, K., Watanabe, N., and Meguro, K. (1991). Polymerization of Styrene Adsolubilized in Polymerizable Surfactant Bilayer on Alumina. Langmuir, 7, 1775.

11. Fuangswasdi, A., Charoensaeng, A., Sabatini, D. A., Scamehorn, J.F., Acosta, E.J., Osathaphan, K., and Khaodhiar, S. (2006). Mixture of Anionic and Cationic Surfactants with Single and Twin Head groups: Solubilization and Adsolubilization of Stytene and Ethylcyclohexane. J. Surfactant and Detergents, 9, 29.

12. Gadelle, F., Wan, J., and Tokunaga, T. K. (2001). Removal of Uranium(VI) from Contaminated Sediments by Surfactants. J. Environ. Qual., 30, 470.

13. Harwell, J. H. (2006). Short Course in Applied Surfactant Science and Technology, Chapter I.G. Surface tension and Wetting.

14. Harwell, J. H., Hoskins, J. C., Schechter, R. S., and Wade, W. H. (1985). Pseudophase Separation Model for Surfactant Adsorption: Isomerically Pure Surfactants. Langmuir, 1, 251.

15. Hirai, Y., Watanabe, T., and Komasawa, I. (2000). Preparation of Semiconductor Nanoparticle-Polymer Composites by Direct Reverse Micelle Polymerization Using Polymerizable Surfactants. J. Phys. Chem., 104, 8962.

16. Kitiyanan, B., O'Haver, J. H., Harwell, J. H., and Osuwan, S. (1996). Absolubilization of Styrene and Isoprene in Cetyltrimethylammonium Bromide Admicelle on Precipitated Silica. Langmuir, 9, 2162.

17. Krajangpan, S. (2004). Enhanced Adsolubilization in Silica-Packed Column by Mixture of Cationic and Anionic Surfactants. Master Thesis, Graduat School, Chulalongkorn University.

18. Lopata, J. J. (1988). A Study of the Adsorption of Binary Anionic Surfactant Mixtures on Alpha Alumina Oxide. Master Thesis, Department of Chemical Engineering, University of Oklahoma.

19. Nayyar, S. P., Sabatini, D. A., and Harwell, J. H. (1994). Surfactant Adsolubilization and Modifiled Admicellar Sorption of Nonpolar, Polar, and Ionizable Organic Contaminants. Envi. Sci . Technol., 28, 1874.

20. Nunn, C. C., Schechter, R. S., and Wade, W. H. (1982). Visual Evidence Regarding the Nature of Hemimicelles through Surface Solubilization of Pinacyanol Chloride. J. Phys. Chem., 86, 3271.

21. Pongprayoon, T., O'Rear, E. A., Yanumet, N., and Yuan, W. (2003). Wettability od Cotton Modified by Admicellar Polymerization. Langmuir, 19, 3770.

22. Rosen, M. J. (1989). Surfactant Phenomena. Wiley, Jonh & Sons, Incoperated.

23. Rouse, J. D., Sabatini, D. A., Deeds, N. E. et al. (1995). Micellar Solubilization of Saturated Hydrocarbon Concentrations As Evaluated by Semiequilibrium Dialysis. Environ. Sci. Technol., 29, 2484.

24. Sabatini, D. A. (2006). Emulsions and Microemulsions. Short Course in Applied Surfactant Science and Technology, Chapter II.A.

25. Sabatini, D. A., Knox, R. K., Harwell, J. et al. (2000). Integrated Design of Surfactants Enhanced DNAPL Remediation: Efficient Supersolubilization and Gradient Systems. Journal of Contaminant Hydrology, 45, 99.

26. Scamehorn, J. F., Schechter, R. S., and Wade, W. H. (1982). Adsorption of Surfactant on Mineral Oxide Surfaces from Aqueous Solutions. I: Isomerically pure anionic surfactants. J. Colloid and Interf. Sci., 85, 463.

27. Somasundaran, P., and Fuerstrnsu, D. W. (1966). Mechanism of Alkyl Sulfonate Adsorption at the Alumina-Water Interface. Journal of Physical Chemistry, 90.

28. Sun, S., and Jaffe, P. R. (1996). Sorption of Phenanthrene from Water onto Alumina Coated with Dianionic Surfactants. Environ. Sci. Technol., 30, 2960.

29. Tamura, H., Knoche, M., and Bukovac, M. J. (2001). Evidence for surfactant solubilization of plant epicuticular wax. J. Agric. Food Chem., 49, 1809.

30. Tan, Y., and O'Haver, J. H. (2004). Lipophilic linker impact on adsorption of and styrene adsolubilization in polyethoxylated octylphenols. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 232, 101.

31. Thakulsukanant, C., Lobban, L. L., Osuwan, S., and Waritswat, A. (1997). Adsolubilization and Stability Characteristics of Hydrocarbon Aggregates Chemically Bonded to Porous Silica. Langmuir, 13, 4595.

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

33. Wu, J., Lee, C., Harwell, J., and O'Rear, E. A. (1989). Adsorbed Surfactant Bilayers as Two-Dimensional Solvents: Surface Modification by Thin-Film Formation. Surfactant-Based Separation Processes, Surfactant Science Series, 33, p.173.