CHAPTER 4

RESULTS AND DISCUSSION

4.1 Adsorption study

The adsorption of single surfactants and three mixture mole fractions of the mixed SHDPDS and DPC surfactants were studied onto positively charged alumina using an electrolyte concentration of 0.015 M NaCl, equilibrium pH of 6.5-7.5 and temperature of 20±2°C. The surfactant adsorption isotherm was plotted on logarithm scale. The maximum adsorption was calculated as the mean value at the plateau region of the surfactant adsorption isotherm. Figure 4.1 is an example of such a surfactant adsorption isotherm.

Since, the maximum adsorption (plateau region) occurs at the CMC of the mixed surfactant system, the CMC values of the surfactant systems were also determined through the surfactant adsorption isotherm. The surfactant molecule per area was calculated assuming that the surfactant molecule had access to the entire alumina surface, with the specific area of alumina being 133 m^2/g (measured by N_2/BET adsorption method). Table 4.1 summaries the experimentally determined CMCs, maximum total surfactant adsorption (average at the plateau region), and surfactant molecule per surface area for SHDPDS, DPC, and their mixtures.

4.1.1 Adsorption of single surfactant system onto alumina for SHDPDS and DPC

The adsorption isotherms of single surfactant systems of SHDPDS and DPC onto positively charged alumina are shown in Figure 4.1. The results show that the adsorptions of SHDPDS and DPC increase with increasing equilibrium surfactant concentration. The maximum adsorption of SHDPDS, 2.4 x 10^{-4} mole/g (1.09 molecule/nm^2), was higher than the maximum adsorption of DPC 3.5 x 10^{-5} mole/g (0.15 molecule/nm^2). The maximum amount of SHDPDS adsorbed is consistent with the results reported by Sun and Jaffe (1996). Sun and Jaffe studied the adsorption of Dowfax 8390 (or SHDPDS) onto aluminum oxide without buffering the pH. They reported that the maximum adsorption of Dowfax 8390 was 61,000 mg/kg (1.82 x10^{-4} mole/g or 0.71 molecule/nm^2, calculated with 155 g/m^2 for alumina as used in their study).

From Figure 4.1, it can be seen that SHDPDS was highly adsorbed onto alumina due to the electrostatic attraction between negatively charged SHDPDS (twin-head anionic surfactant that contains two-negatively charged head group) and positively charged alumina. On the other hand, the adsorption of DPC was very low due to the electrostatic repulsion between like charged cationic surfactant head group and positively charged alumina. Nonetheless, there are small amounts of DPC adsorbed onto alumina, possibly due to counterions effect on the adsorption of cationic surfactant onto alumina. The counter ions (0.015 M NaCl as used in this study) reduced the electrostatic repulsion between positively charged cationic surfactants and positively charged alumina. Addition of neutral electrolyte causes a decrease in the adsorption of ionic surfactants onto oppositely charged adsorbent and an increase in their adsorption onto a similarly charged adsorbent (Rosen, 1989). Alumina surfaces at solution pH of 6.5 -.7.5, which is two pH units below the PZC of alumina, probably has negative sites for the adsorbed cationic surfactants.

4.1.2 Adsorption of mixed anionic and cationic surfactant system onto alumina for SHDPDS and DPC

Adsorption of the three SHDPDS and DPC mole fractions of 3:1, 10:1 and 30:1 were conducted to investigate the synergistic effect of mixed anionic and cationic surfactant adsorption onto alumina as shown in Figure 4.2 at electrolyte concentration of 0.015 M NaCl, equilibrium pH of 6-5-7.5, and temperature of 20± 2°C. The total surfactant adsorption was plotted versus the total equilibrium concentration for the three mole fractions for SHDPDS and DPC. The total adsorption of the mixed surfactants increased as the total surfactant increased in concentration, reaching a maximum adsorption for all surfactant mixtures. The amount of adsorbed surfactant in the plateau maximum adsorption region increased with increasing cationic surfactant molar ratio as shown in Figure 4.3. While the mixed surfactant system of 3:1 SHDPDS:DPC molar ratio provided the highest amount of adsorbed surfactants onto alumina, this maximum total surfactant adsorption (3.10×10^{-4} mole/g for 3:1 SHDPDS: DPC molar ratio) was only 25% percent higher than the SHDPDS alone (2.4×10^{-4} mole/g). The maximum surfactant adsorption versus anionic/cationic surfactant molar ratio in the mixed surfactant system are shown in Figure 4.3

Figure 4.4 shows the adsorption of SHDPDS alone and for the three mixture mole fractions of SHDPDS and DPC onto alumina. The results show that the adsorption of SHDPDS increased with increasing equilibrium surfactant concentration. However, the maximum SHDPDS adsorption in the three mixed surfactant systems was virtually the same. Thus, it can be seen that there is no significant increase in the SHDPDS adsorbed with additional of DPC.

The adsorption of DPC alone and for the three mixture mole fractions of SHDPDS and DPC are also shown in Figure 4.5. It is interesting to note that at the same SHDPDS concentration, the DPC adsorption increased as the DPC mole fraction in the surfactant mixture was increased, and that this increase was most dramatic for low surfactant concentrations.

From the adsorption of individual anionic and cationic surfactants in the mixed surfactant system, it can be inferred that the anionic surfactants readily adsorbed onto alumina due to the electrostatic attraction between two negatively charged head anionic surfactant. At the same time, it appears that the positively charged alumina does in fact contain a number of negatively charged sites that account for the adsorption of cationic surfactants onto the alumina, even at a pH of 7 which is two pH units below the PZC. Capovila et al. (2000) studied the formation of mixed anionic and cationic surfactant adsorbed onto laponite clay at solution pH of 8.5. They found that cationic surfactant head groups adsorbed onto negatively charged clay and provided hydrophobic layers for adsorbed hydrophobic tails of anionic surfactants.

4.2 Solubilization study

Before looking at the adsolubilization into adsorbed surfactant, the solubilization of organic solute into surfactant micelles was investigated to allow a comparison between the two types of aggregates. The study of the solubilization potentials (ability to enhance organic solute in solution) of single surfactants and the three mixture mole fractions for

SHDPDS and DPC were conducted with styrene and ethylcyclohexane at electrolyte concentration of 0.015 M NaCl and temperature of 20 ± 2 °C. Solubilization isotherms were plotted with organic solute solubilization versus aqueous surfactant concentration in the solution in logarithm scale. The transition point was determined as the CMC of each surfactant mixtures. Table 4.2 shows the CMC values of single surfactants and the three surfactant mixture mole fractions (which were determined experimentally from Figure 4.6 and Figure 4.7). It can be seen that the CMC values of each surfactant varied with presence of the organic solutes. Rosen (1989) reports that surfactant CMC values are impacted by solubilization of organic solutes could change because the activity of the surfactant is changed by the introduction of organic solutes.

The micellar partitioning coefficient (K_{mic}) describes the partitioning of the various organic solutes into the micelle (Edwards et al., 1991). K_{mic} is defined as

$$K_{mic} = \frac{X_{mic}}{X_{aq}} \tag{4.1}$$

where;

X_{mic} is the mole fraction of the organic solute in the micelle pseudophase.

X_{aq} is the mole fraction of the organic solute in the aqueous phase.

The mole fraction are calculated as

$$X_{mic} = \frac{C_0 - C_{eq}}{(C_0 - C_{eq}) + (S_0 - S_{eq})} \tag{4.2}$$

$$X_{aq} = \frac{C_{eq}}{C_{eq} + 55.55} \tag{4.3}$$

where:

C_0 = the concentration of organic solute at initial
C_{eq} = the concentration of organic solute at equilibrium
S_0 = the concentration of surfactant at initial
S_{eq} = the concentration of surfactant at equilibrium
55.55 = represents 1/molar volume for water

The partitioning of organic solutes is described by the molar solubilization ratio (MSR), which is the slope of the solubilization isotherm beyond the CMC value (see Figures 4.8 and 4.9). MSR indicates the moles of organic solute in the micelle per moles of micellar surfactant. Table 4.2 summarizes the molar solubilization ratio and K_{mic} of this study. MSR determinations were determined based on straight-line function with r^2 regression greater than 0.97. The mole fraction of the organic solute in micelles is related to MSR by the simple relationship (Rouse et al., 1995).

$$X_{mic} = \frac{MSR}{(1 + MSR)} \tag{4.4}$$

$$K_{mic} = \frac{MSR/(1 + MSR)}{C_{eq}/(C_{eq} + 55.55)} \tag{4.5}$$

From MSR values in Figure 4.8 and Figure 4.9, the result shows that the MSR for both styrene and ethylcyclohexane increased with increasing surfactant concentration. The order of solubilization potential (MSR) is DPC <SHDPDS< 30:1< 10:1 <3:1 SHDPDS:DPC molar ratio. This trend is observed for the solubilization of both styrene and ethylcyclohexane by SHDPDS and DPC. The solubilization potential of styrene and ethylcyclohexane by SHDPDS is greater than DPC. This is likely because the cationic head group is larger and more electrostatic, producing a less desirable structure for solubilization.

The second trend was observed in the mixed surfactant system. The solubilization potential increased with increasing a mole ratio of cationic surfactant in the surfactant mixtures for both styrene and ethylcyclohexane system. As the cationic surfactant concentration increased, the electrostatic repulsion between anionic surfactant head group was reduced. Micelles form more easily and the packing density (aggregation number) increase due to the reduction in electrostatic repulsion between the head groups reducing the electrical potential in micelles, and providing a more favorable environmental for the organic solute.

It can be seen that the solubilization potential of ethylcyclohexane is higher than styrene for the SHDPDS and the three mixtures mole fractions. The MSR value of ethylcyclohexane is about 3 times that of styrene. The ethylcyclohexane showed much greater partitioning because the hydrophobicity of ethylcyclohexane (log K_{ow}= 4.40) is higher than styrene (log K_{ow} = 2.95). Thus, the partitioning of ethylcyclohexane into hydrophobic site of micelles became more favorable.

4.3 Adsolubilization Studies

The adsolubilization isotherm of styrene and ethylcyclohexane by SHDPDS and the three mixture feed mole fractions for SHDPDS and DPC onto alumina are shown in Figure 4.10 and 4.11, respectively at electrolyte concentration of 0.015 M NaCl, equilibrium pH of 6.5-7.5, and temperature of 20±2 °C. Styrene is a polar organic solute and ethylcyclohexane is a non-polar organic solute, which is expected to partition into the palisade region and the core of the admicelles, respectively.

The admicellar partition coefficient (K_{adm}) is analogous to the micellar partition coefficient (Nayyar et al., 1994).

$$K_{adm} = \frac{X_{adm}}{X_{aq}} \tag{4.6}$$

where

X_{adm} is the mole fraction of organic solute in the admicelle phase

X_{aq} is the mole fraction of organic solute in the aqueous phase

For this study, X_{adm} values are calculated as:

$$X_{adm} = \frac{(C_{i,S} - C_{f,S})}{(C_{i,S} - C_{f,S}) + (S_{i,AIS} + S_{f,AIS}) + (S_{i,CIS} + S_{f,CIS})} \tag{4.7}$$

where:

X_{adm} = Mole fraction of organic solute in admicelle

$C_{i,S}$ = Initial concentration of organic solute (M)

$C_{f,S}$ = Final concentration of organic solute (M)

$S_{i,AIS}$ = Initial concentration of anionic surfactant, (M)

$S_{f,AIS}$ = Final concentration of anionic surfactant, (M)

$S_{i,CIS}$ = Initial concentration of cationic surfactant, (M)

$S_{f,CIS}$ = Final concentration of cationic surfactant, (M)

4.3.1 Styrene Adsolubilization

The adsolubilization isotherms of styrene by SHDPDS and SHDPDS-DPC mixtures are shown in Figure 4.10. The results show that the amount of adsolubilized styrene increased with increasing equilibrium styrene concentration for all adsolubilization isotherms. As expected, the styrene adsolubilization reached a maximum as the styrene concentration reaches its water solubility, with the concentration of surfactant below its CMC. Figure 4.11 also shows the adsolubilized styrene by the mixed anionic and cationic surfactant system for different mole fractions of cationic surfactants in the surfactant mixtures. It can be seen that the styrene admicellar mole fraction becomes less favorable with increasing the mole fraction of cationic surfactants in the mixtures. As the concentration of cationic surfactant increased, the net electrostatic charge of the anionic surfactant head group is reduced, which should facilitate the incorporation of polar organic solute into the palisade region of admicelles. In the palisade region, the cationic surfactants attach to the adsorbed anionic surfactants. As a result, the polar organic solute, styrene, which is expected to adsolubilize into the palisade layer of admicelles, is then squeezed out. The admicellar partition coefficient (K_{adm}) values for styrene adsolubilization in SHDPDS and the three mixture mole fractions as shown in Table 4.2 are determined by the slope of adsolubilization isotherm (Figure 4.11). In order to gain insight into locus of adsolubilization of styrene in the mixed surfactant admicelle, The X_{adm}/X_{aq} of styrene (calculated from Equations 4.6 and 4.7) versus equilibrium styrene concentrations are shown in Figure 4.12. The The X_{adm}/X_{aq} slowly decreases with increasing equilibrium styrene concentration, supporting that the polar styrene is adsolubilized into the palisade region of the surfactant admicelles (Nayyar et al., 1994; Dickson and O'Haver, 2002). However, Kitiyanan et al. (1996) studied the adsolubilization of styrene by a cetyltrimethylammonium bromide (CTAB) bilayer onto precipitated silica. The results showed that the styrene adsolubilization constant is unchanged with increasing equilibrium styrene concentration in the aqueous phase, suggesting that the styrene was adsolubilized in the both the core and the palisade region of the admicelles.

4.3.2 Ethylcyclohexane Adsolubilization

The adsolubilization isotherms of ethylcyclohexane by SHDPDS and SHDPDS-DPC mixtures are shown in Figure 4.13. The results show that the amount of adsolubilized ethylcyclohexane increased with increasing equilibrium ethylcyclohexane concentration for all adsolubilization isotherms. Figure 4.13

also shows the adsolubilized ethylcyclohexane by the mixed anionic and cationic surfactant system with different mole fractions of cationic surfactant in the mixtures. It can be seen that the ethylcyclohexane admicellar mole fraction became more favorable with increases in the mole fraction of cationic surfactants in the mixtures. However, the adsolubilization of ethylcyclohexane appears to be independent of the cationic surfactant mole fraction in 30:1 SHDPDS:DPC molar ratio. The admicellar partition coefficient (K_{adm}) values for ethylcyclohexane, as shown in Table 4.2, were determined from slopes in the adsolubilization isotherm (Figure 4.14). For locus of adsolubilization of ethylcyclohexane, Figure 4.15 shows X_{adm}/X_{aq} of ethylcyclohexane versus ethylcyclohexane concentration at equilibrium. The X_{adm}/X_{aq} of ethylcyclohexane at low ethylcyclohexane concentration loading increased with increasing equilibrium ethylcyclohexane concentration and then slowly decreased at the high concentration. At low ethylcyclohexane concentration suggested that the non-polar ethylcyclohexane adsolubilized into the core of the admicelles. However, it is not clear why the X_{adm}/X_{aq} ratio decreased at the high ethylcyclohexane concentration.

From the mixed anionic and cationic surfactant adsorption study, it is suggested that the adsorbed anionic surfactant molecules lie flat on alumina surface at a low surfactant concentration, and provided hydrophobic sites, as the tail group of anionic surfactants facing to aqueous solution. The interactions of hydrophobic tail groups increase with increasing surface coverage. The schematic illustration, with mixed anionic and cationic surfactant adsorption and adsolubilization, helps to explain our results as shown in Figure 4.16. In this structure, two-negatively charged head groups of anionic surfactant are adsorbed onto the positively charged alumina surface with hydrophobic tail groups facing into the aqueous phase and leading to anionic and cationic surfactant bilayers. As cationic surfactant molecules increase, the hydrophobic site in the core region increases which in turn promotes the adsolubilization of non polar ethylcyclohexane in the admicelle. When the cationic surfactant present in the system, it decreases the net charge of the surface, thereby making the core more hydrophobic and promoting the formation of denser aggregates, both of which would increase hydrophobic adsolubilization. Thus, increasing cationic surfactant mole fraction in the mixed anionic and cationic surfactant systems promotes adsolubilization into the core region and resists the adsolubilization into the palisade region by changing the nature of the adsorbed surfactant aggregates.

From the partition coefficient values in the solubilization and adsolubilization studies, it is observed that the K_{mic} values for styrene and ethylcyclohexane in solubilization study are the same order as the corresponding K_{adm} values in adsolubilization study, but consistently lower. This could be due to the higher packing density of the admicelles which are fixed on the solid surface, than that of the micelles. Recent research study found nearly identical micellar and admicellar partitioning for organic solutes (Park, and Jaffe, 1993; Rouse et al., 1993). Park and Jaffe (1993) also found that organic solute partitioning into micelles/admicelles was proportional to the mass of surfactant molecules. However, the point to be addressed here is that admicellar partitioning in adsolubilization can be as attractive as micellar uptake in solubilization for organic solutes. This phenomenon can be useful in environmental applications.

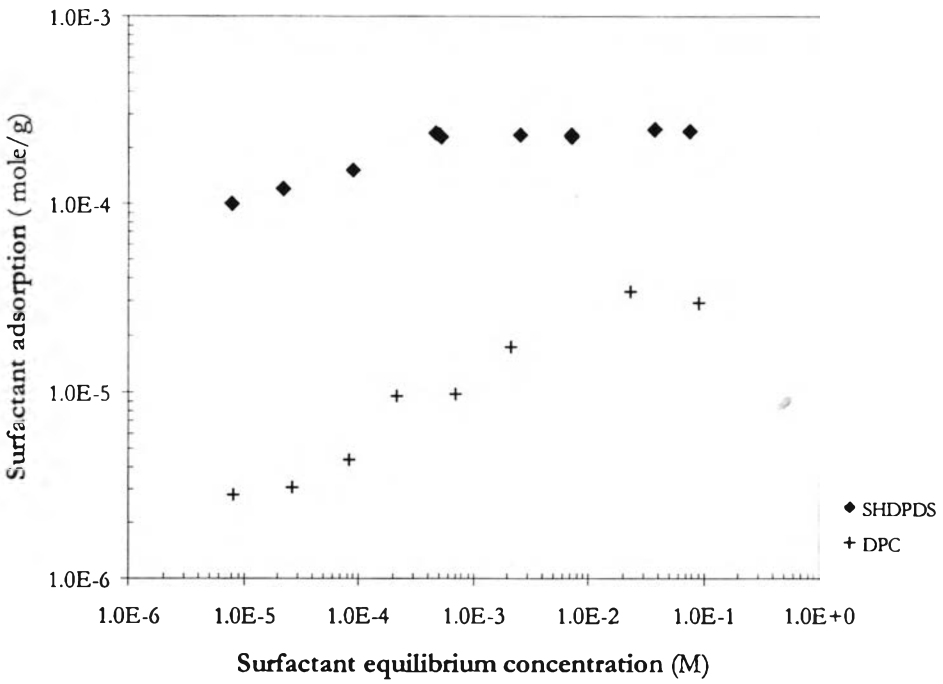

Figure 4. 1 The adsorption isotherm of SHDPDS and DPC onto alumina at electrolyte concentration of 0.015 M NaCl, equilibrium pH of 6.5-7.5 and temperature of 20±2°C.

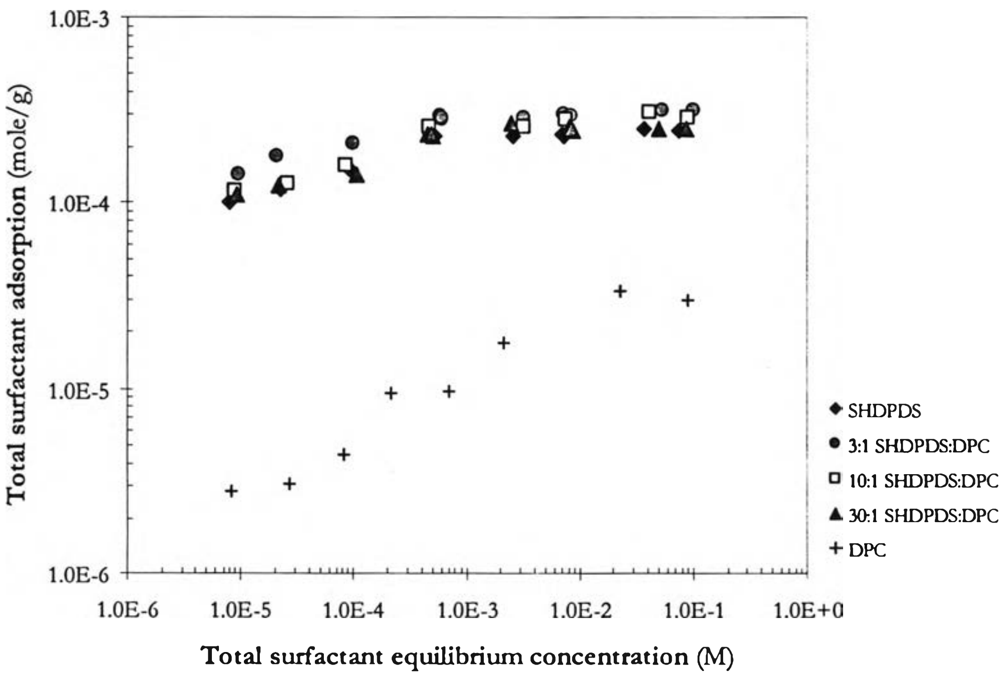

Figure 4. 2 The single surfactants and three mixture mole fractions for SHDPDS and DPC adsorption onto alumina at electrolyte concentration of 0.015 M NaCl, equilibrium pH of 6.5-7.5, and temperature of 20±2°C.

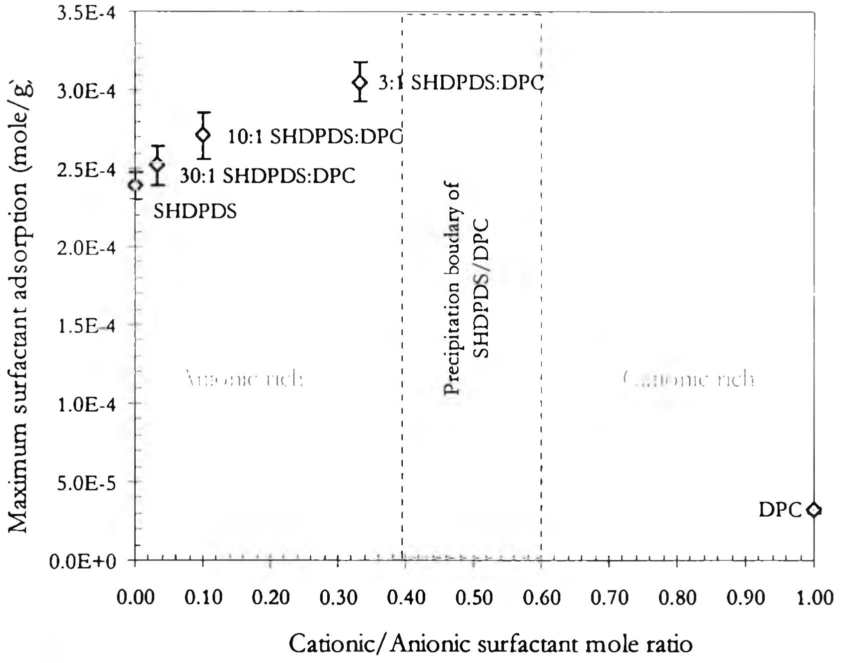

Figure 4. 3 Maximum surfactant adsorption and cationic/anionic surfactant molar ratio

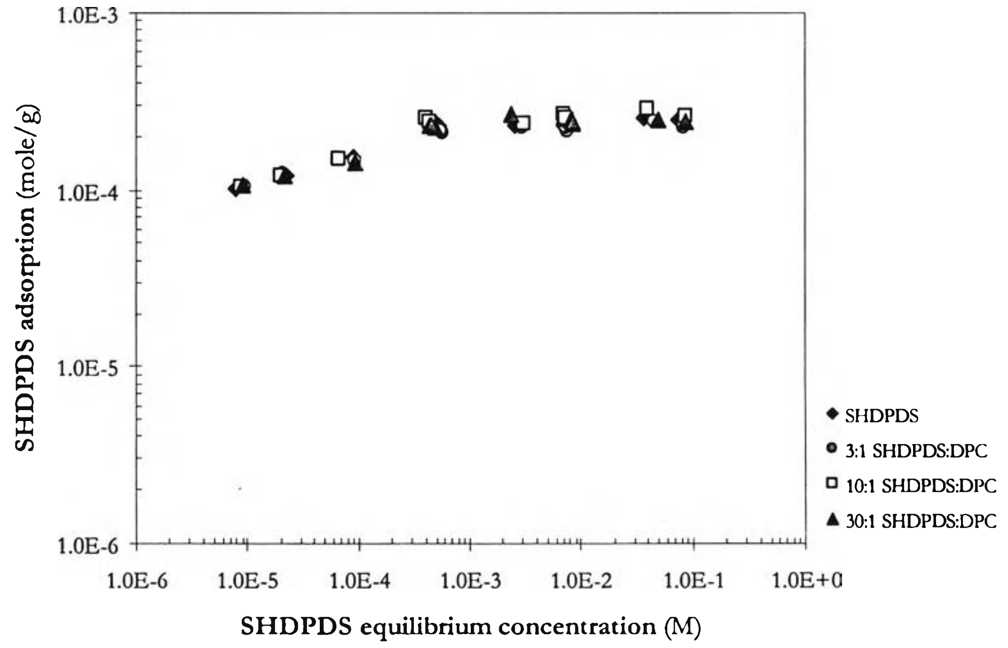

Figure 4. 4 SHDPDS adsorption for SHDPDS alone and for three mixture mole fractions of SHDPDS and DPC onto alumina at electrolyte concentration of 0.015 NaCl, equilibrium of pH 6-5-7.5, and temperature of 20±2 °C.

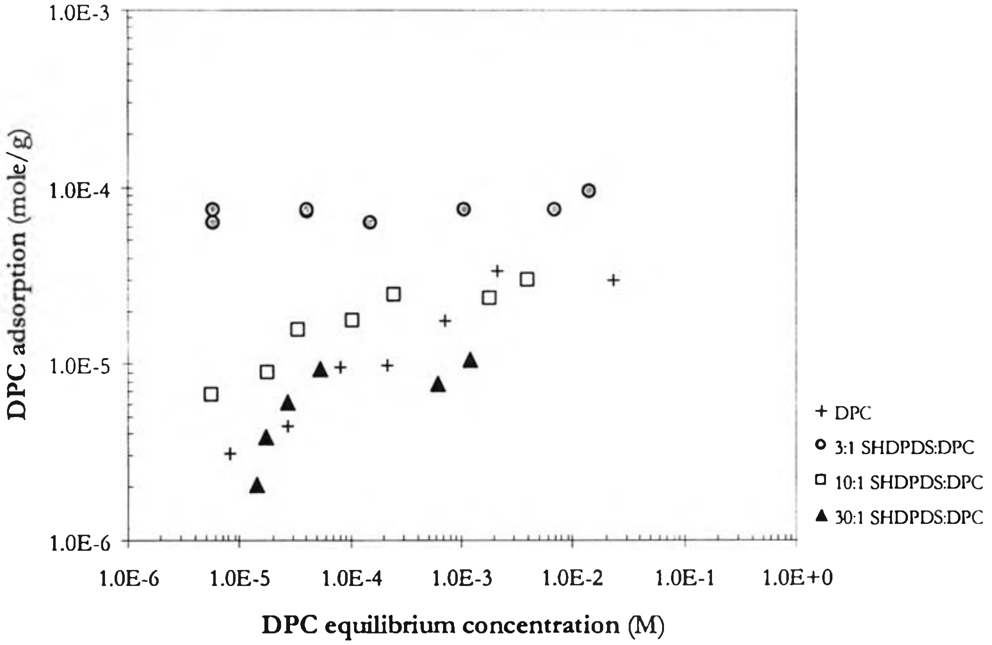

Figure 4. 5 DPC adsorption for DPC alone and for three mixture mole fractions of SHDPDS and DPC onto alumina at electrolyte concentration of 0.015 M NaCl, equilibrium pH of 6.5-7.5, and temperature of 20±2 °C.

Table 4. 1 Experimentally determined CMCs, the maximum total adsorption, and molecule per area of single surfactants and three mixture mole fractions for SHDPDS and DPC system.

Surfactants	**Experimentally determined CMC** (mM)	**Max. total adsorption** (mmole/g)	**Area per molecule** (molecule/nm^2)
SHDPDS	0.49	0.239	1.09
30:1 DPDS:DPC	0.46	0.252	1.15
10:1 DPDS:DPC	0.43	0.278	1.26
3:1 DPDS:DPC	0.55	0.301	1.36
DPC	-	0.031	0.10

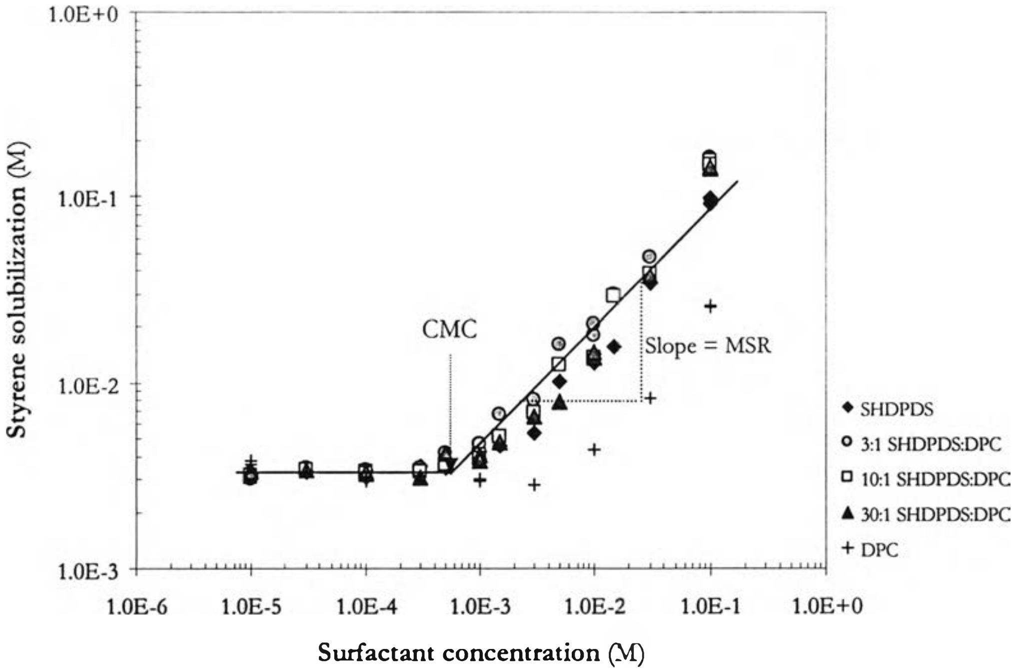

Figure 4.6 Solubilization isotherm of styrene by single surfactant and three mixture feed mole fractions for SHDPDS and DPC at electrolyte concentration of 0.015 M NaCl

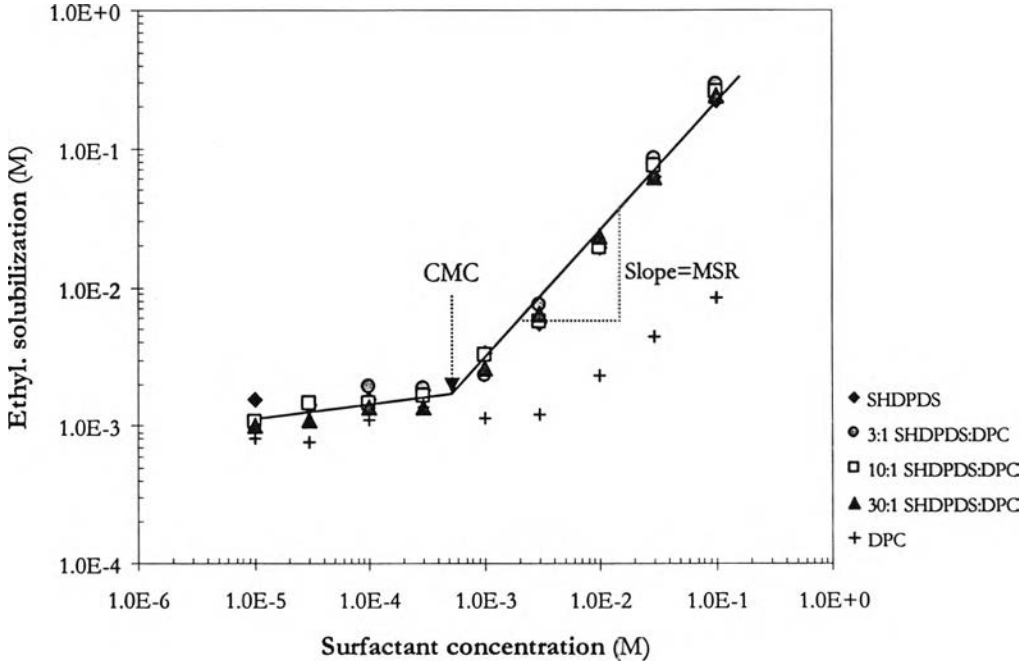

Figure 4. 7 Solubilization isotherm of ethylcyclohexane by single surfactant and three mixture feed mole fractions for SHDPDS and DPC at electrolyte concentration of 0.015 M NaCl

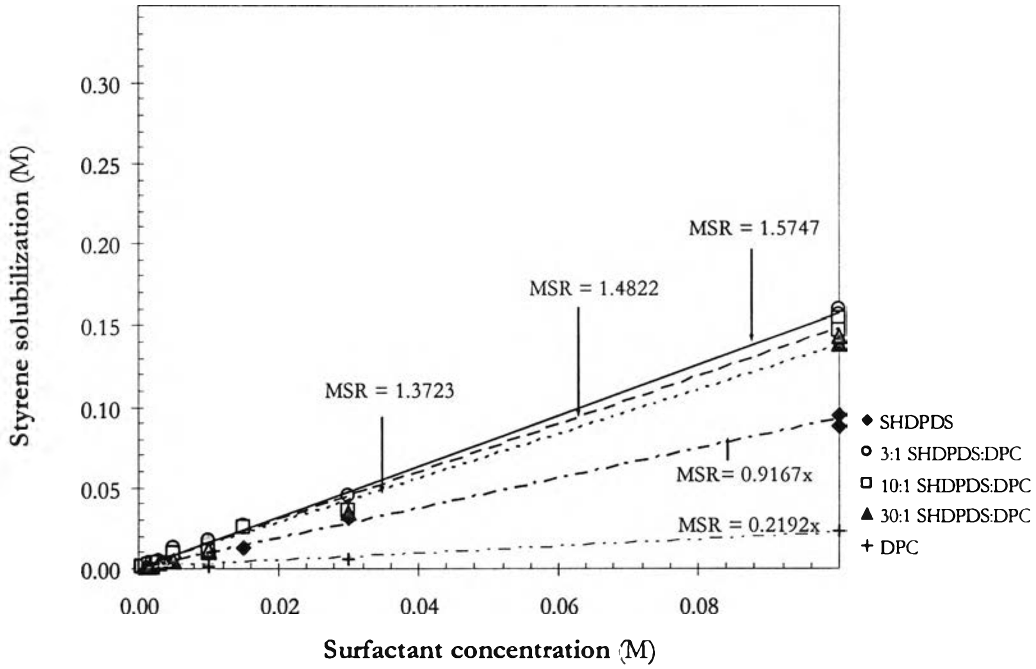

Figure 4. 8 Molar surfactant ratio (MSR) of styrene for single surfactant and three mixture mole fractions for SHDPDS and DPC

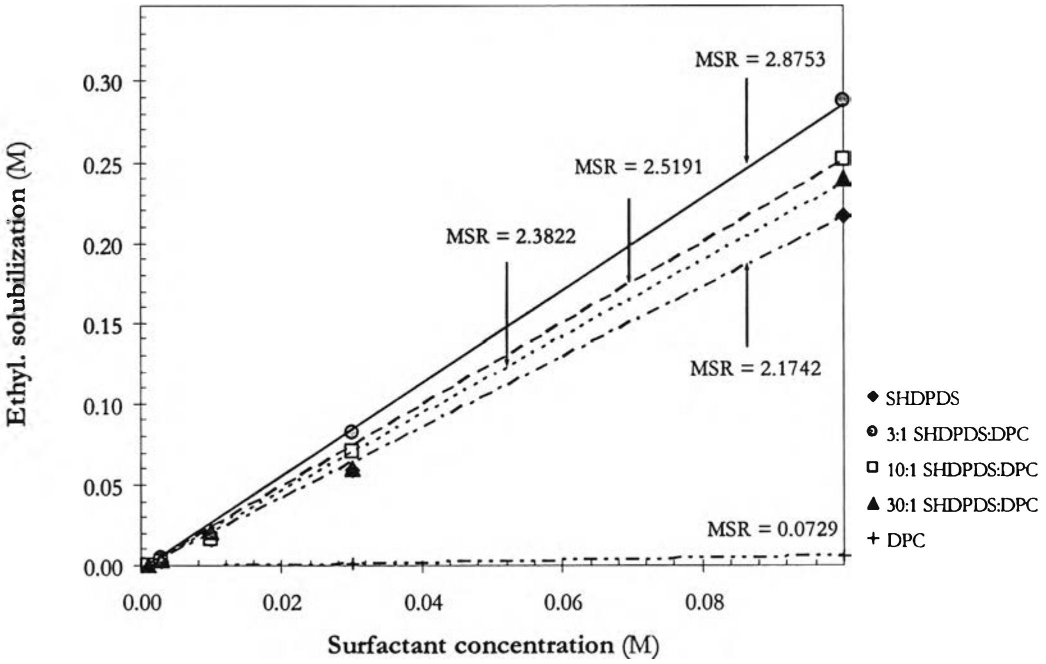

Figure 4. 9 Molar surfactant ratio (MSR) of ethylcyclohexane for single surfactant and mixture feed mole fractions for SHDPDS and DPC

Table 4. 2 CMC of surfactant, MSR value from solubilization study, and partitioning values obtained in this study

Surfactant	Log K_{ow}	CMC mM	S_{cmc} mM	MSR	Log K_{mic}	Log K_{adm}
Styrene	2.95					
SHDPDS		1.00	3.46	0.9154	3.88	4.52
DPDS:DPC 30:1		1.10	3.48	1.3710	3.96	-
DPDS:DPC 10:1		0.90	3.44	1.4822	3.98	4.36
DPDS:DPC 3:1		0.80	3.52	1.5734	3.99	4.37
DPC		4.00	3.17	0.2216	3.50	-
Ethylcyclohexane	4.40					
SHDPDS		0.80	1.59	2.1716	4.38	4.92
DPDS:DPC 30:1		0.70	1.56	2.3848	4.51	4.90
DPDS:DPC 10:1		0.60	1.41	2.5191	4.45	4.91
DPDS:DPC 3:1		0.80	1.21	2.8720	4.42	4.91
DPC		2.00	1.06	0.0729	3.55	-

S_{cmc} – organic solute concentration at CMC of surfactant

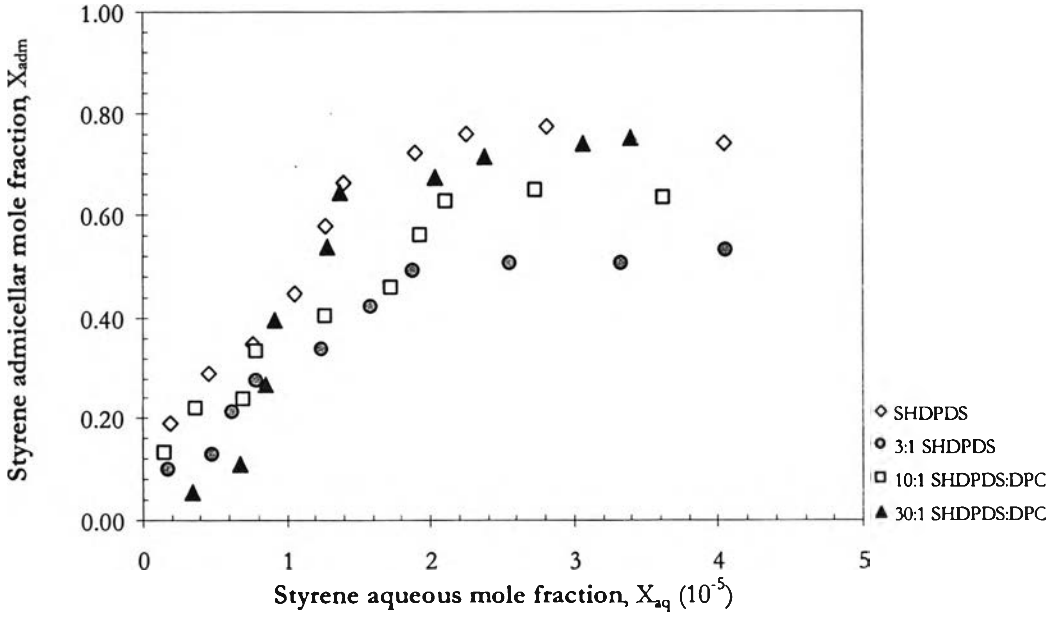

Figure 4. 10 Adsolubilization of styrene by SHDPDS and three mixture mole fractions for SHDPDS and DPC at electrolyte concentration of 0.015 M NaCl, equilibrium pH 6.5-7.5 and temperature of 20±2 °C

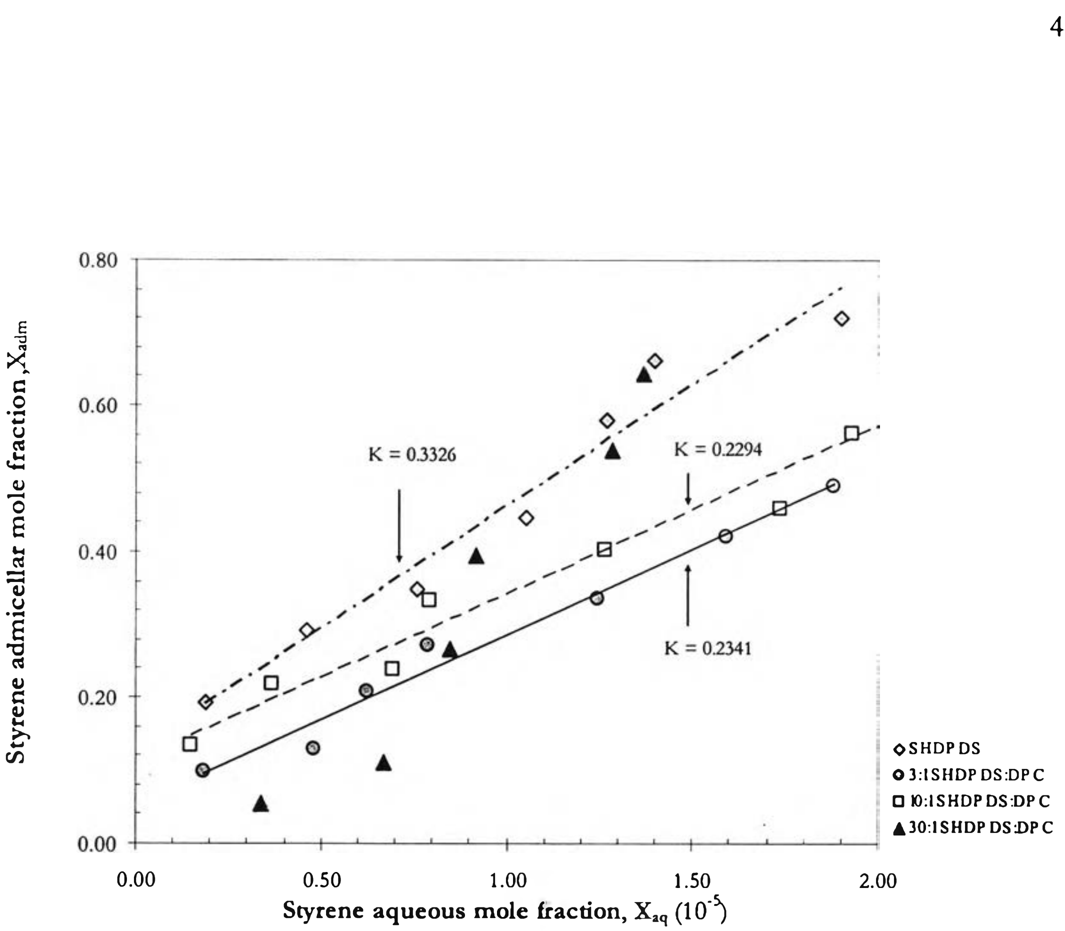

Figure 4. 11 Styrene admicellar partition coefficient (K_{adm}) by SHDPDS and three mixture mole fractions for SHDPDS and DPC.

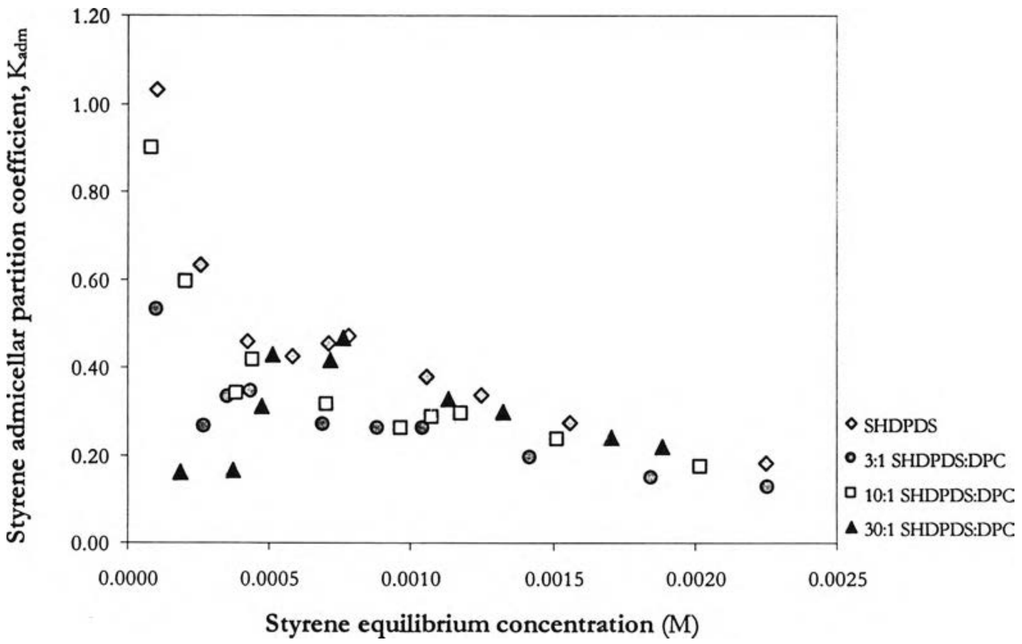

Figure 4. 12 Ploted X_{adm}/X_{aq} of styrene versus styrene concentration at equilibrium for SHDPDS and three mixture mole fractions for SHDPDS and DPC.

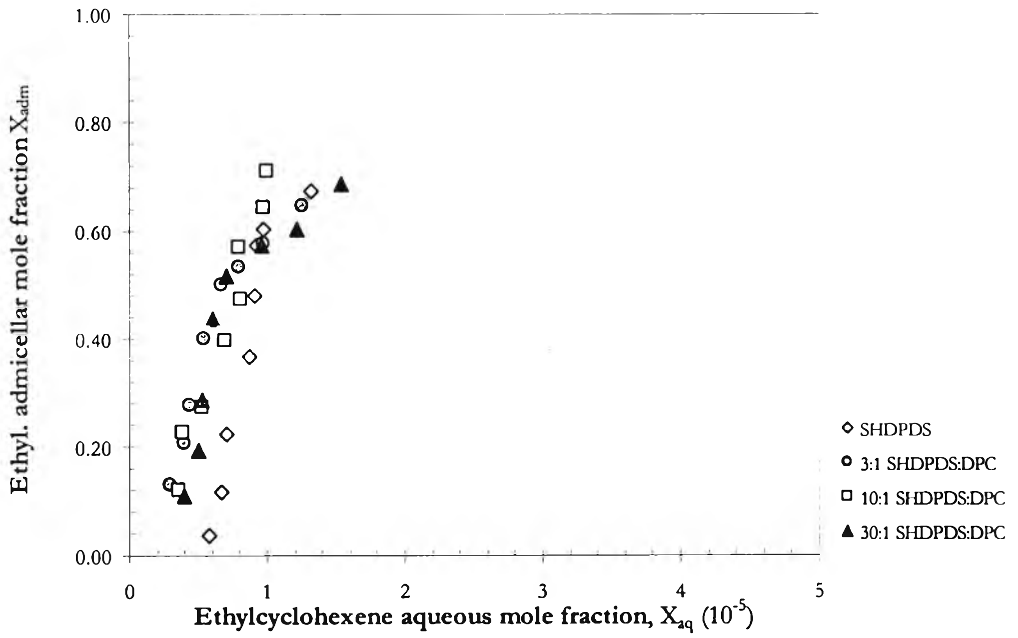

Figure 4. 13 Adsolubilization of ethylcyclohexane by SHDPDS and three mixture mole fractions for SHDPDS and DPC at electrolyte concentration of 0.015 M NaCl, equilibrium pH of 6.5-7.5 and temperature of 20±2 °C

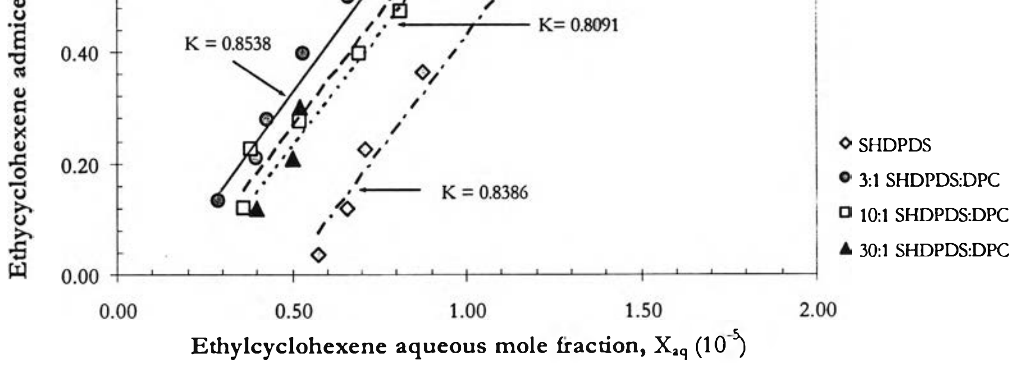

Figure 4. 14 Ethylcyclohexane admicellar partition coefficient (K_{adm}) for SHDPDS and three mixture mole fractions for SHDPDS and DPC

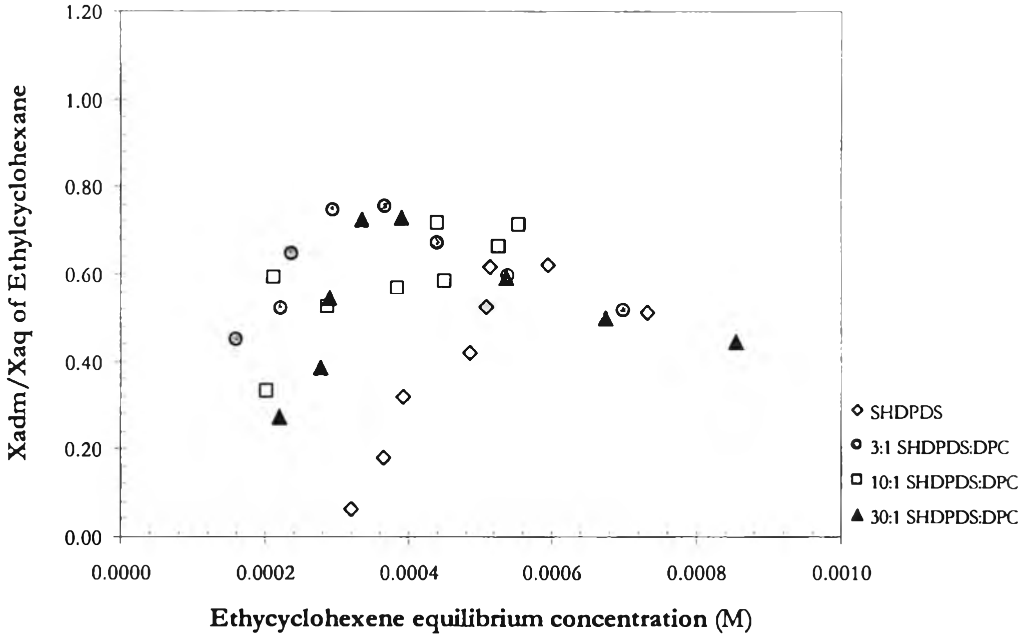

Figure 4. 15 Plotted X_{adm}/X_{aq} of ethylcyclohexane versus ethylcyclohexane concentration at equilibrium by SHDPDS and for three mixture mole fractions for SHDPDS and DPC

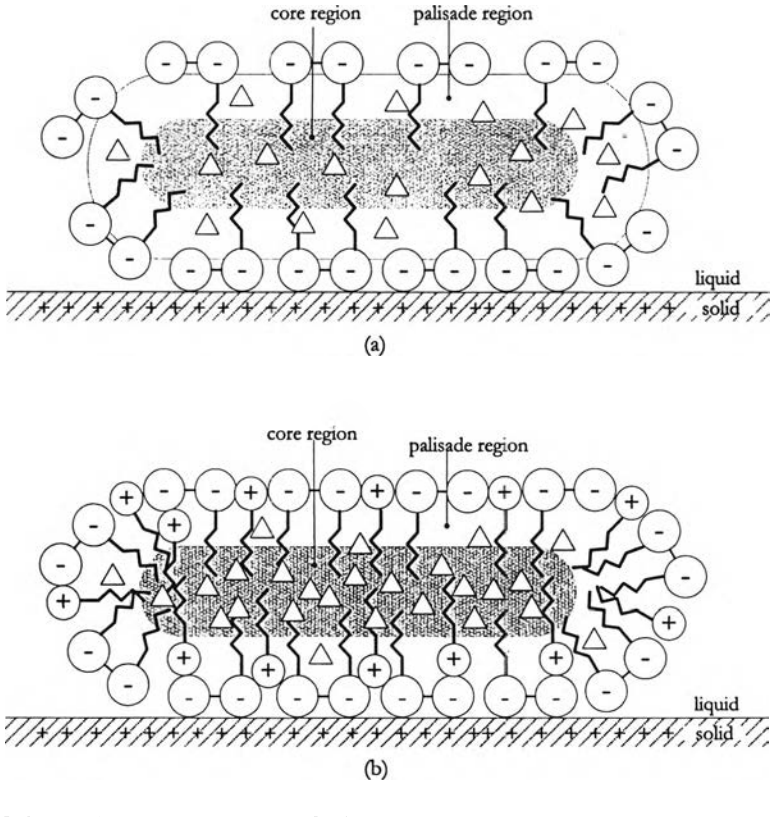

Figure 4. 16 Schematic representation of adsolubilization in (a) twin-head anionic surfactant (SHDPDS) and (b) mixed anionic and cationic surfactant (SHDPDS and DPC) aggregates onto positively charge alumina