



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Determination Critical Micelle Concentration (CMC) of Surfactant

Critical micelle concentrations of (1) the single surfactant systems: the cationic surfactant, cetyltrimethyl ammonium bromide (CTAB); the anionic surfactant, sodium dodecyl sulfate (SDS); the nonionic surfactant, polyoxyethylene octyl phenol ether (OPEO₁₀ or Triton X-100); and the triblock copolymer, Pluronic L64 (PEO₁₃PPO₃₀PEO₁₃), and (2) the mixed surfactant systems: the cationic surfactant–triblock copolymer, cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64; the anionic surfactant–triblock copolymer, sodium dodecyl sulfate (SDS)–Pluronic L64; the nonionic surfactant–triblock copolymer, polyoxyethylene octyl phenol ether (Triton X-100)–Pluronic L64, were determined by plotting the surfactant concentration versus surface tension for both the single and mixed systems.

From previous study it was found that the concentration of surfactant with maximum amount of surfactant adsorbed on the solid surface is likely to be equal to critical micelle concentration (CMC) (Rosen, 2004). Thus, in this research, the surface tension was to be measured to determine the critical micelle concentration (CMC) to identify the concentration of surfactant used for studying of adsorption of surfactant on solid surface. Surface tension decreased sharply when the surfactant concentration increased at the beginning and then the surface tension hardly changed even the surfactant concentration increase further. The critical micelle concentration (CMC) can be detected from the change in the slope of the experimental surface tension, γ , data graph which becomes almost constant. The best linear fit to the descending and horizontal line of the plot was obtained, and their intersection was used to calculate the critical micelle concentration (CMC).

In many process, two surfactants are used together to improve the efficiency of the system. According to the previous research, it was found that using block copolymer in adsolubilization can improve the amount of organic adsolubilization when compare with conventional surfactants (Arunwuttipong *et al.*, 2006 and Pathamaporn *et al.*, 2008). And using mixed surfactant can adsorb larger amount of

organic than using single surfactant. In this research, block copolymer mix with conventional surfactant will be employed to determine their efficiency for adsorption of organic substances. The ratio of mixed surfactant between conventional surfactant to block copolymer was 7 to 1. This is because at this ratio the lowest amount conventional surfactant to use for getting lowest critical surfactant concentration (CMC).

4.1.1 Determination of critical micelle concentration (CMC) of the single cationic surfactant; cetyltrimethyl ammonium bromide (CTAB)

The surface tension versus concentration curve for cetyltrimethyl ammonium bromide (CTAB) is shown in Figure 4.1. The result shows that the critical micelle concentration (CMC) of the CTAB is approximately 0.86 mM, which smoothly correlates to value suggested by Gao *et al.* (2004).

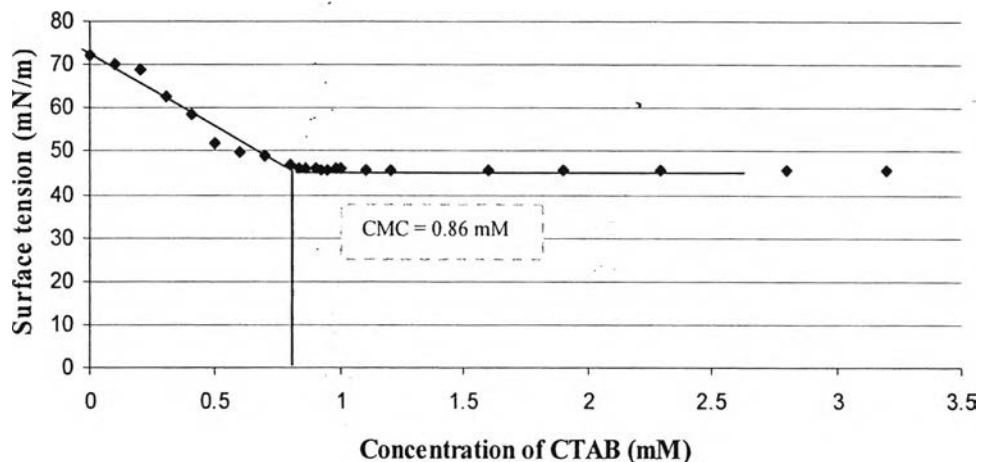


Figure 4.1 Surface tension versus concentration curve for cetyltrimethyl ammonium bromide (CTAB) at 30°C.

4.1.2 Determination of critical micelle concentration (CMC) of the single anionic surfactant; sodium dodecyl sulfate (SDS)

The surface tension versus concentration curve for sodium dodecyl sulfate (SDS) is shown in Figure 4.2. The result shows that the critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) is about 7.8 mM, which is closely correlated to the literature value of 8.0 mM (Pispas *et al.*, 2006).

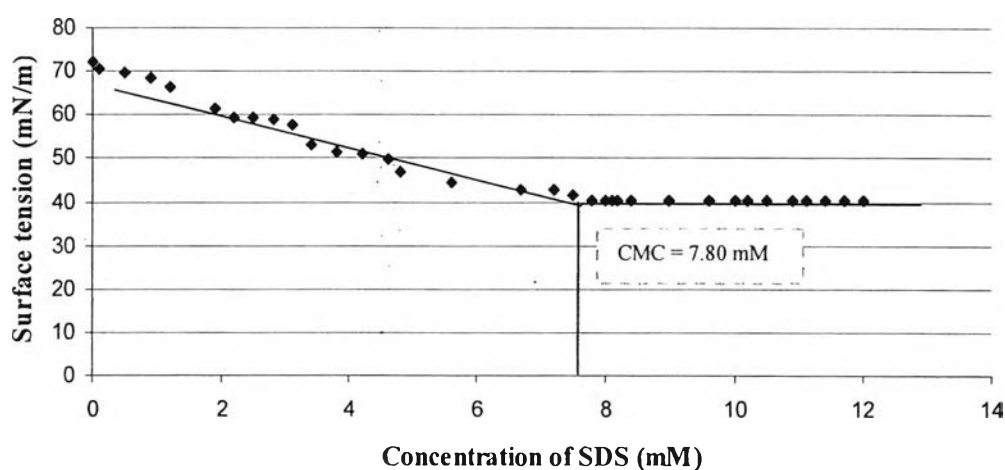


Figure 4.2 Surface tension versus concentration curve for sodium dodecyl sulfate (SDS) at 30°C.

4.1.3 Determination of critical micelle concentration (CMC) of the single nonionic surfactant: polyoxyethylene octyl phenol ether (OPEO₁₀, or Triton X-100)

The surface tension versus concentration curve for polyoxyethylene octyl phenol ether (OPEO₁₀, or Triton X-100) is shown in Figure 4.3. The result shows that the critical micelle concentration (CMC) of polyoxyethylene octyl phenol ether (OPEO₁₀, or Triton X-100) is approximately 0.24 mM, which is relatively close to the literature value of 0.22 mM (Yu *et al.*, 2007).

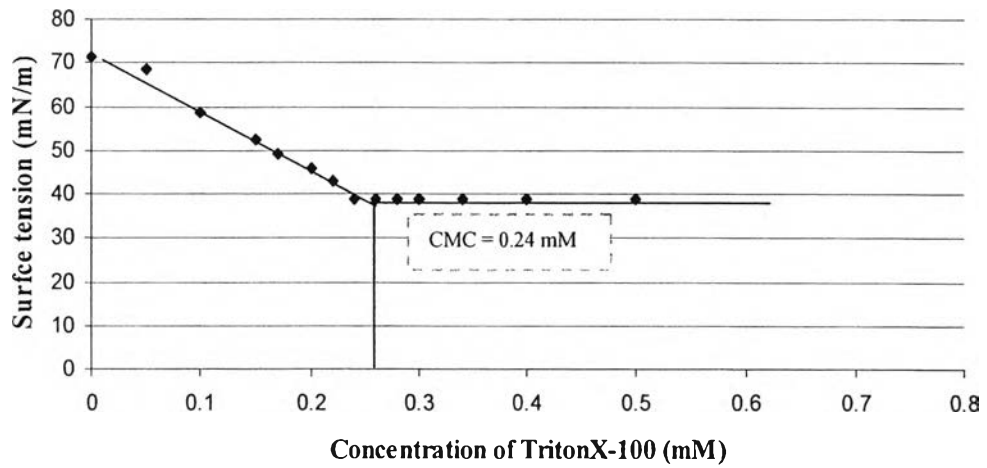


Figure 4.3 Surface tension versus concentration curve for polyoxyethylene octyl phenol ether (OPEO₁₀, or Triton X-100) at 30°C.

4.1.4 Determination of critical micelle concentration (CMC) of the single triblock copolymer; Pluronic L64 (PEO₁₃PPO₃₀PEO₁₃)

The surface tension versus concentration curve for the triblock copolymer, Pluronic L64, is shown in Figure 4.4. The result shows that the critical micelle concentration (CMC) of the triblock copolymer, Pluronic L64 (PEO₁₃PPO₃₀PEO₁₃), is approximately 1.72 mM, which correlates to the literature value of 1.76 mM (Yu *et al.*, 2007).

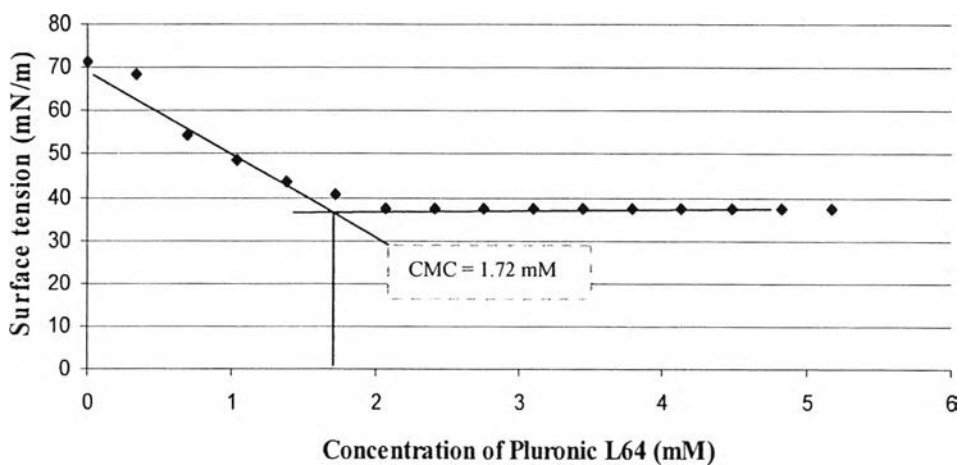


Figure 4.4 Surface tension versus concentration curve for Pluronic L64.

4.1.5 Determinaion of critical micelle concentration (CMC) of the mixed system of the cationic surfactant; cetyltrimethyl ammonium bromide (CTAB), and the triblock copolymer, Pluronic L64 ratio 7:1

The critical micelle concentration of the mixed surfactant system, cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64, was determined at 30°C from the surface tension measurement. Figure 4.5 shows the surface tension versus concentration curve for the mixed surfactant system, and the critical micelle concentration (CMC) was equal to 0.83 mM. The surface tension of the mixed surfactant—cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64— solution decreased sharply at low concentration and reached a constant value when concentration of the mix surfactant concentration was equal to 44.74 mN/m.

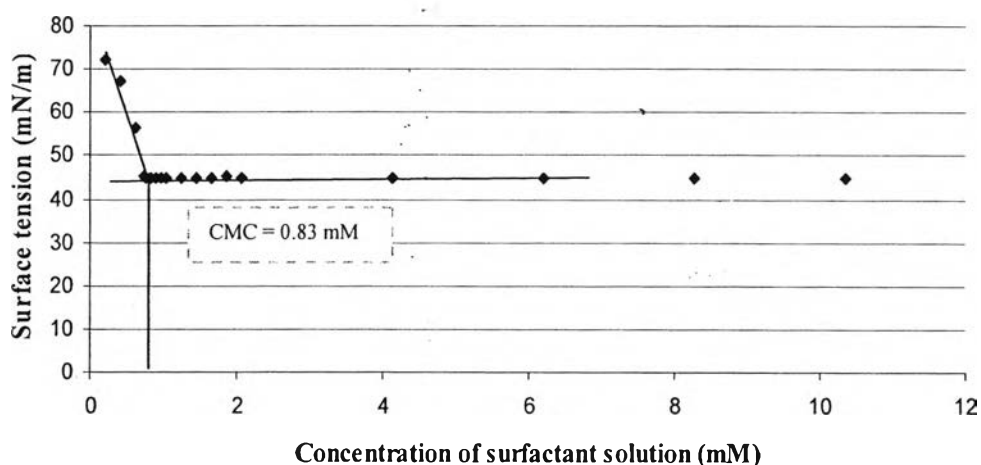


Figure 4.5 Surface tension versus concentration curve for Pluronic L64 mixed with CTAB.

4.1.6 Determinaion of critical micelle concentration (CMC) of the mixed surfactant system of the anionic surfactant, sodium dodecyl sulfate (SDS) and the triblock copolymer, Pluronic L64 ratio 7:1

The critical micelle concentration of the mixed surfactant system—triblock copolymer, Pluronic L64, and the anionic surfactant, sodium dodecyl sulfate (SDS)—was determined by plotting the surface tension versus concentration curve,

as shown in Figure 4.6. The result shows that the mixed critical micelle concentration (CMC) of the sodium dodecyl sulfate (SDS) and the triblock copolymer, Pluronic L64 ($\text{PEO}_{13}\text{PPO}_{30}\text{PEO}_{13}$), was 6.83 mM.

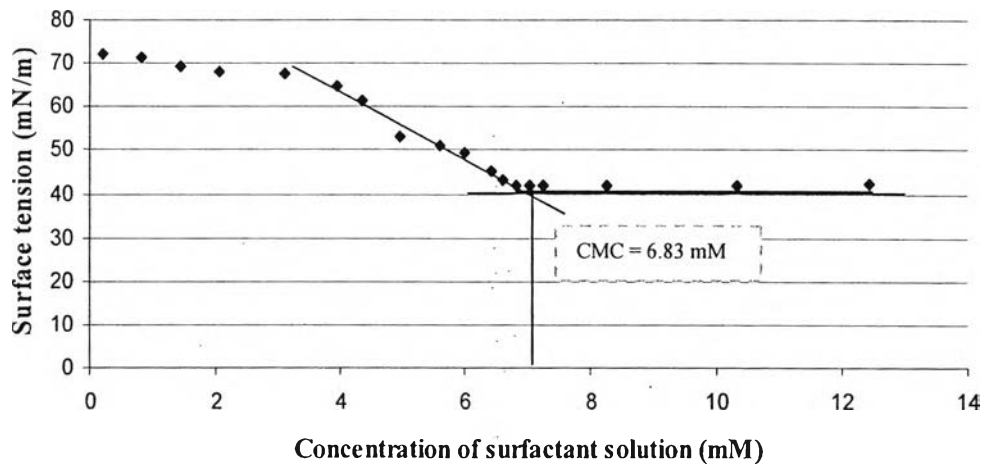


Figure 4.6 Surface tension versus concentration curve for Pluronic L64 mixed with SDS.

4.1.7 Determination of critical micelle concentration (CMC) of the mixed surfactant system of the nonionic surfactant, polyoxyethylene octyl phenol ether (OPEO₁₀, or Triton X-100), and the triblock copolymer, Pluronic L64 ratio 7:1

In the nonionic-nonionic mixed surfactant system, Triton X-100–Pluronic L64, the formation of mixed micelles occurred and the critical micelle concentration (CMC) of this mixed surfactant system was measured, as shown in Figure 4.7. The result shows that the critical micelle concentration of this mixed nonionic system was about 2.48 mM.

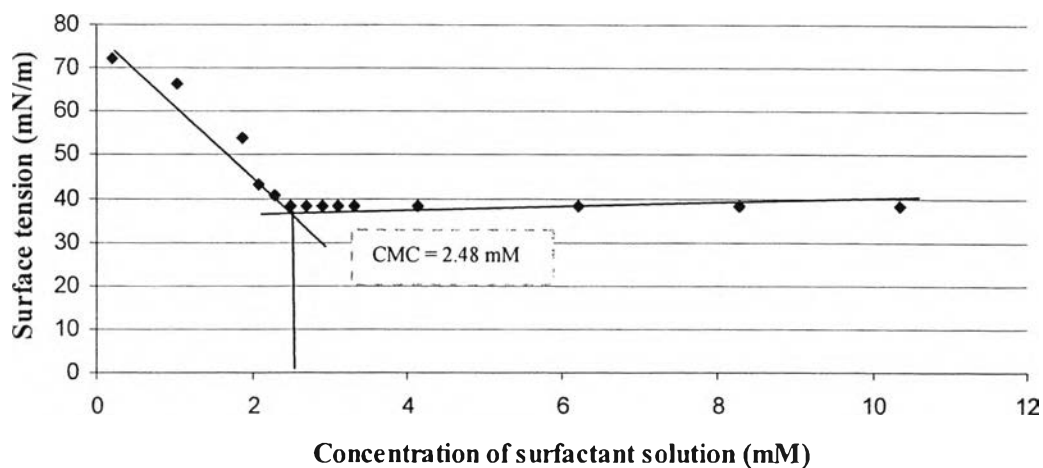


Figure 4.7 Surface tension versus concentration curve for Pluronic L64 mixed with Triton X-100.

The surface tension of the surfactant solutions, both for the single surfactant systems and the mixed surfactant systems, at different concentrations were measured and plotted versus concentration of surfactant solution. The point at which the surface tension levels off when the increasing surfactant concentration was taken is called the critical micelle concentration (CMC). The surface tension of a surfactant at CMC, γ_{CMC} , indicates the ability of a surfactant to lower the surface tensions, and accordingly the CMC indicates its efficiency.

In the case of the single systems in this study, the CMC value of SDS, Pluronic L64, CTAB, and Triton X-100 appear to be about 7.80, 2.06, 0.92, and 0.24 mM, respectively, which are close to the reported literature values. It can be noted that surface tension, γ , of the ionic surfactants in the presence of micelles is higher than that of the nonionic surfactants, except for the Pluronic L64, which is a nonionic surfactant in polymer form.

In the case of mixed surfactants, the CMC value could be higher or lower than critical micelle concentration (CMC) of the single surfactant systems, depending on the interaction between Pluronic (block copolymer) and conventional surfactant which was mixed with Pluronic in the mixture. Pluronics can bind with both anionic and cationic surfactants. For the mixed CTAB–Pluronic L64 surfactant system, both CMC of each single surfactant CTAB (0.92 mM) and Pluronic L64

(2.06 mM) are higher than CMC of mixed surfactant CTAB–Pluronic L64 (0.83 mM). Relatively similar to the above system, both CMC of each single surfactant SDS (7.80 mM) and Pluronic (2.06 mM) is higher than CMC of the mixed surfactant SDS–Pluronic L64 (6.83 mM). From the literature synergism, it was suggested that, synergism occurred in an aqueous system containing two surfactants when a given surface tension can be attained a total mixed surfactant concentration lower than that of each surfactant (Rosen, 2004). Thus, for the CTAB–Pluronic L64 and the SDS–Pluronic L64 mixed systems, they exhibited synergism as a decreasing surface tension at the air-solution interface. The synergism of the mixed surfactant system of the ionic surfactant and the nonionic triblock copolymer surfactant is due to their interaction to form different packings. These packings depend on the nature of the head group of the hydrocarbon surfactant (Meta et al., 2007). Whereas in the case of the Triton X-100 and Pluronic L64, there is an antagonistic effect was observed, this is because its CMC value of the mixed surfactant system (0.83 mM) presents higher CMC value than the CMC value of individual surfactant each.

4.2 Surfactant Adsorption onto Silica

In this part of the study, the adsorption of the single surfactant systems onto silica at 30°C was studied. The adsorption isotherm of each surfactant was plotted on a log-log scale. The isotherm shows the characteristic ‘s’ shape. The surfactant adsorption increased with increasing equilibrium surfactant concentration and then leveled off at a high equilibrium surfactant concentration. TOC and UV-Vis spectrophotometry were used to determine adsorption by analyzing the amount of surfactant concentration remained in the solution.

4.2.1 Adsorption isotherm of the single anionic surfactant, sodium dodecyl sulfate (SDS) on silica

For the sodium dodecyl sulfate (SDS) adsorption, the experimental result showed that there was no adsorption of SDS on the silica surface. Palida *et al.* (2007) reported that anionic surfactants do not adsorb on a silica surface. This was due to the repulsion between the charge of head group of SDS and the negative charge on the silica.

Comparing the SDS adsorption onto alumina, Amalia *et al.* (2007) found that the highest amount of SDS adsorbed was about 210 mg g^{-1} , depending on the density of the positive charges on the alumina.

The adsorbed surfactant concentration and the amount of adsorbed surfactant were calculated using equations below:

Adsorbed surfactant concentration (mol/dm^3) = Total surfactant concentration before adsorption (M) – Surfactant concentration at equilibrium (M)

Amount of adsorbed surfactant (g/ g of silica) = [Adsorbed surfactant concentration (mol/dm^3) * 10^{-3} cm^3 * Volume of surfactant (cm^3) * Molecular weight of surfactant]/ amount of silica (g)

4.2.2 Adsorption isotherm of the single cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) on silica

The amount of CTAB adsorbed on the silica surface at 30°C without the presence of an additive was measured. The adsorption isotherm was plotted for the amount of surfactant adsorbed on the solid surface versus the equilibrium concentration on a log-log scale, as shown in Figure 4.8. The adsorption isotherm was sigmoidal with a rapid increase of amount adsorbed slightly below its CMC with stabilization at higher concentration. The adsorption isotherm represents the characteristic II, III, and IV regions (see Figure 2.3). Region IV of the adsorption isotherm is commonly a plateau region above the CMC. It also shows a maximum that is slightly above CMC. The CMC value has been determined from the adsorption isotherm of CTAB, fitting the data using linear equations. While Nontasorn *et al.* (2005) reported the CMC of CTAB was $900 \mu\text{M}$, the value obtained from the adsorption isotherm in this study was shown to be $855 \mu\text{M}$. This CMC value was in good agreement with the literature value.

Comparing to the SDS adsorption on the silica, a significant amount of CTAB was adsorbed on the solid surface due to the opposite charged surface. The maximum surfactant adsorption occurs at the equilibrium concentration of $850 \mu\text{M}$

and the maximum adsorbed surfactant is 317.42 mmol of surfactant per gram of silica. Therefore, the adsorption isotherm obtained in this study indicated that CTAB surfactants preferentially adsorb onto the silica.

Compared to the adsorption of nonionic surfactants such as Triton X-100, the CTAB adsorption is considered to be through electrostatic interaction between the positive charge of the CTAB head groups and the negative charge of the silica surface. The electrostatic attraction with the cationic CTAB will be dominant at low CTAB concentration. At high CTAB concentration, the CTAB adsorbs through the hydrocarbon chain-chain interaction with neighboring CTAB (Parida *et al.*, 2006).

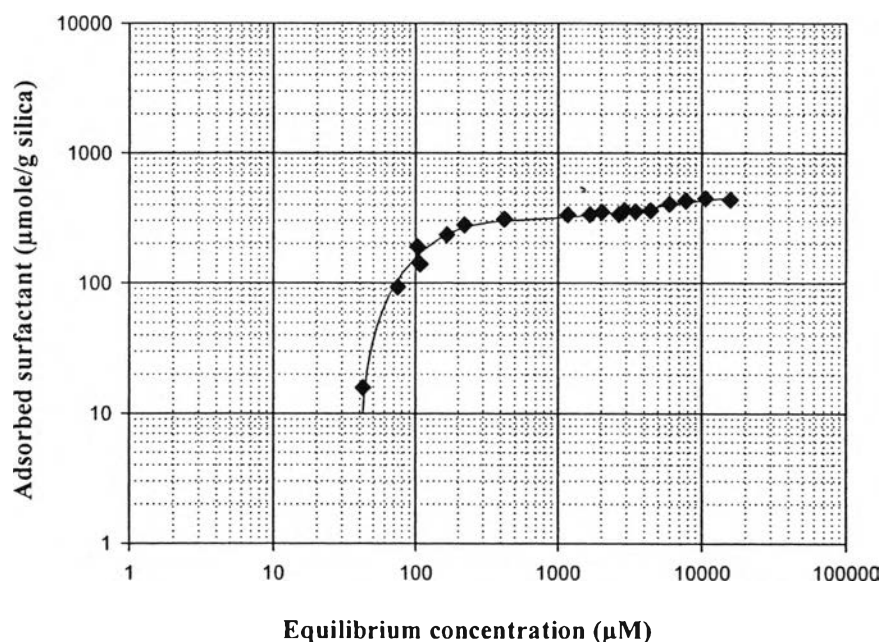


Figure 4.8 Adsorption isotherm of CTAB on the silica at 30°C.

4.2.3 Adsorption isotherm of the single nonionic surfactant, polyoxyethylene octyl phenol ether (OPEO₁₀ or Triton X-100) on silica

The amount of Triton X-100 adsorbed on the silica surface at 30°C was measured. The adsorption isotherm was plotted for the amount of surfactant

adsorbed on the solid surface versus the equilibrium concentration on a log-log scale, as shown in Figure 4.9. The adsorption isotherm shows the characteristic 'S' shape. The adsorbed amount steeply increased at the low-concentration regime and reached a plateau value. It showed that Triton X-100 was strongly associated with silica surface. However, the maximum amount of Triton X-100 (283.33 mmol of surfactant per gram of silica) adsorbed on the silica was lower than the maximum amount of CTAB (317.42 mmol of surfactant per gram of silica) adsorbed on the silica.

The CMC value could be estimated from the concentration at the intercept between the linear extrapolations of the rapidly increasing amount of surfactant and of the almost-horizontal line at high surfactant concentration (Wang *et al.*, 2005). The maximum surfactant adsorption occurred at the equilibrium concentration of 0.294 mM and the maximum adsorbed surfactant was 283.33 mmol of surfactant per gram of silica. The CMC value of Triton X-100 obtained in this study at 30°C was in good agreement with the values reported in the literature, which was 240 μ M and 300 μ M, respectively (Mahanajan *et al.*, 2005 and Arunwuttipong *et al.*, 2006).

The adsorption mechanism of Triton X-100 at the silica-water interface was considered to be hydrogen bonding rather an electrostatic interaction because the Triton X-100 is a nonionic surfactant. The hydrogen bonding occurs between the ether oxygen of the surfactant and the surface hydroxyl group of the silica (Esumi *et al.*, 2001).

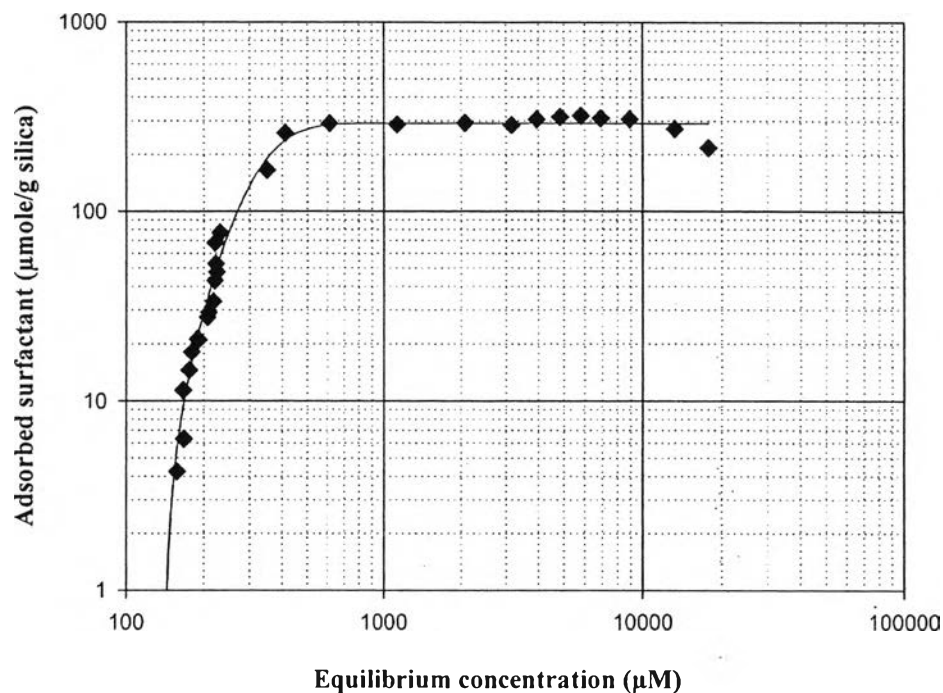


Figure 4.9 Adsorption isotherm of Triton X-100 on the silica at 30°C.

4.3 Adsolubilization of Organic compounds

Three model organic aromatic compounds were selected (phenol, 2-naphthol, and naphthalene) and chosen as organic solutes in the study of adsorption by mixed surfactant systems: cationic surfactant–triblock copolymer, cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64 (mixture A); anionic surfactant–triblock copolymer, sodium dodecyl sulfate (SDS)–Pluronic L64 (mixture B); and nonionic surfactant–triblock copolymer, polyoxyethylene octyl phenol ether (Triton X-100)–Pluronic L64 (mixture C). The reason for selection of CTAB SDS and Triton X-100 as the conventional surfactants is because these CTAB and SDS surfactants have similar type of hydrophobic tails with different polar head, which affects their aggregation properties. Triton X-100, which is also a conventional surfactant, has the relatively similar structure to Pluronic L64 block copolymer.

The critical micelle concentration (CMC) of each mixed surfactant systems measured in the early part of this study was used as the surfactant feed concentration in the adsolubilization of model organic compounds.

Asvapathanagul *et al.* (2005) found that factors affecting the adsolubilization of organic compounds by using adsorbed surfactant onto solid surface are pH of the surfactant solution, ionic strength of the aqueous phase, the type of structural group on the substrate surface, also the molecular structures and types of the surfactants and the solutes. Therefore, the three model organic aromatic compounds (phenol, 2-naphthol, naphthalene) were chosen to provide better understanding of different adsolubilized organic compounds by mix surfactant systems. Comparing among different organic model compounds, phenol was the smallest in size. 2-naphthol and naphthalene were relative similar structure and size but larger than phenol. When comparing between 2-naphthol and naphthalene, 2-naphthol was found to be higher polar than naphthalene because of its side group; methyl group (c.f to naphthalene which has no side group). Phenol is the highest polar solute among three organic compounds because of its hydroxyl group; –OH group.

4.3.1 Adsolubilization of phenol

The amount of adsolubilized phenol versus its reduced bulk concentration (equilibrium concentration/maximum water solubility) is shown in Figure 4.10. The data illustrates that the maximum phenol adsolubilized in the adsorbed layers of the triblock copolymer, Pluronic L64; cationic surfactant–triblock copolymer, cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64 (mixture A); anionic surfactant–triblock copolymer, sodium dodecyl sulfate (SDS)–Pluronic L64 (mixture B); nonionic surfactant–triblock copolymer, polyoxyethylene octyl phenol ether (Triton X-100)–Pluronic L64 (mixture C) are 2.410, 3.120, 2.080, and 1.790 mmol of phenol/g of silica, respectively.

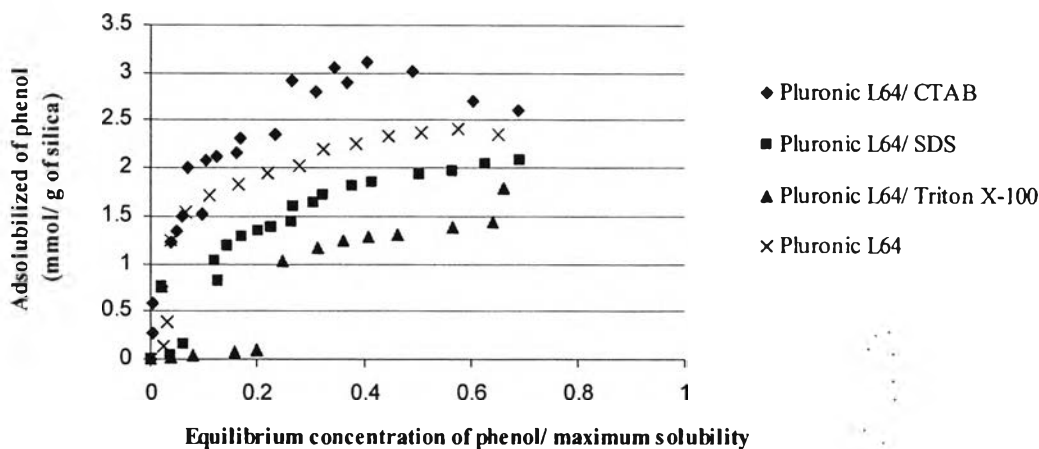


Figure 4.10 Adsolubilization of phenol in the different surfactant systems.

The adsolubilization of phenol increases with increasing equilibrium concentration of phenol for all systems. In the mixed surfactant system CTAB–Pluronic L64 (mixture A), the adsolubilization of phenol is the highest, whereas the lowest is observed in the mixed surfactant system of Triton X-100–Pluronic L64 (mixture C). The results suggested that the adsolubilization of phenol may be related to the amount of adsorbed surfactant as the amount of adsorbed cationic surfactant–triblock copolymer, cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64 (mixture A), is higher than other surfactant systems (mixture B, mixture C, Pluronic L64) since the adsolubilization is related to the amount of adsorption surfactant onto the solid surface (Rosen, 2004). In addition, the adsolubilized phenol capacity also bases on its chemical structure; small size, low number of aromatic ring, and polarity. Thus, the adsolubilized of phenol capacity is relatively higher than the other types of organic aromatic compound. Phenol structure has only one aromatic ring so it adsolubilizes easily into adsorbed surfactant layer. Normally, organic solute adsorbed into core region which is a hydrophobic part. For phenol, not only adsolubilize into core region part but also into palisade part because of hydroxyl side group of its structure. Some part of phenol can be able to adsoulubilize in palisade region. That's why the adsolubilized phenol capacity is rather higher than the others. However, the organic adsolubilization

be able to adsorb in palisade region. That's why the adsorbed phenol capacity is rather higher than the others. However, the organic adsorption capacity has limitation. In the case of using the mixed surfactant between CTAB-Pluronic L64 (mixture A), phenol can adsorb very well. And the capacity uptakes until the limited level, then both core region and palisade region cannot store adsorbed phenol anymore. So when phenol concentration increased after the limitation level, the adsorbed phenol capacity tended to decrease somewhat.

4.3.2 Adsorption of 2-naphthol

Figure 4.11 shows the amounts of 2-naphthol adsorbed into the adsorbed surfactant layers on hydrophobic modified silica particles as the amount of adsorbed 2-naphthol versus its reduced bulk concentration. The data illustrate that the maximum 2-naphthol adsorbed in the adsorbed layers of triblock copolymer, Pluronic L64; cationic surfactant-triblock copolymer, cetyltrimethyl ammonium bromide (CTAB)-Pluronic L64 (mixture A); anionic surfactant-triblock copolymer, sodium dodecyl sulfate (SDS)-Pluronic L64 (mixture B); and nonionic surfactant-triblock copolymer, polyoxyethylene octyl phenol ether (Triton X-100)-Pluronic L64 (mixture C) are 0.195, 0.254, 0.115, and 0.047 mmol of 2-naphthol/g of silica, respectively.

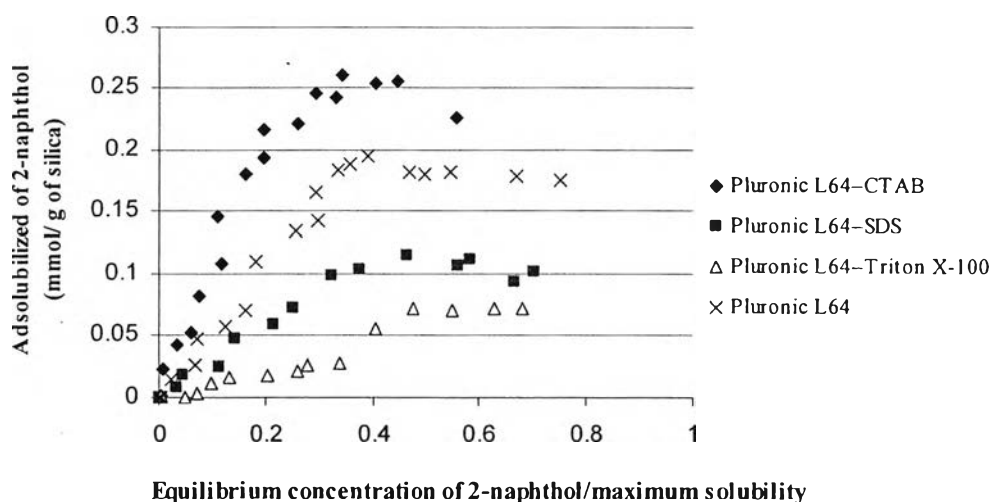


Figure 4.11 Adsolubilization of 2-naphthol in the different surfactant systems.

The adsolubilization of 2-naphthol increased with increasing equilibrium concentration of 2-naphthol for all systems. In the mixed surfactant system SDS–Pluronic L64, the adsolubilization of naphthalene is the highest, whereas the lowest is observed in the mixed surfactant systems of Triton X-100–Pluronic L64. The results suggested that the adsolubilization of the amount of adsorbed cationic surfactant–triblock copolymer; cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64 (mixture A), is higher than other surfactant systems (mixture B, mixture C, Pluroinc L64) since the adsolubilization is related to the amount of adsorption surfactant as the amount of (Rosen, 2004).

4.3.3 Adsolubilization of naphthalene

The amount of adsolubilized naphthalene versus its reduced bulk concentration (Equilibrium concentration/maximum water solubility) is shown in Figure 4.12. The data illustrates that the maximum phenol adsolubilized in the adsorbed layers of triblock copolymer, Pluronics L64; cationic surfactant–triblock copolymer, cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64 (mixture A); anionic surfactant–triblock copolymer, sodium dodecyl sulfatate (SDS)–Pluronic L64 (mixture B); and nonionic surfactant–triblock copolymer, polyoxyethylene octyl

phenol ether (Triton X-100)–Pluronic L64 (mixture C) are 0.017, 0.023, 0.010, and 0.004 mmol of naphthalene/g of silica, respectively.

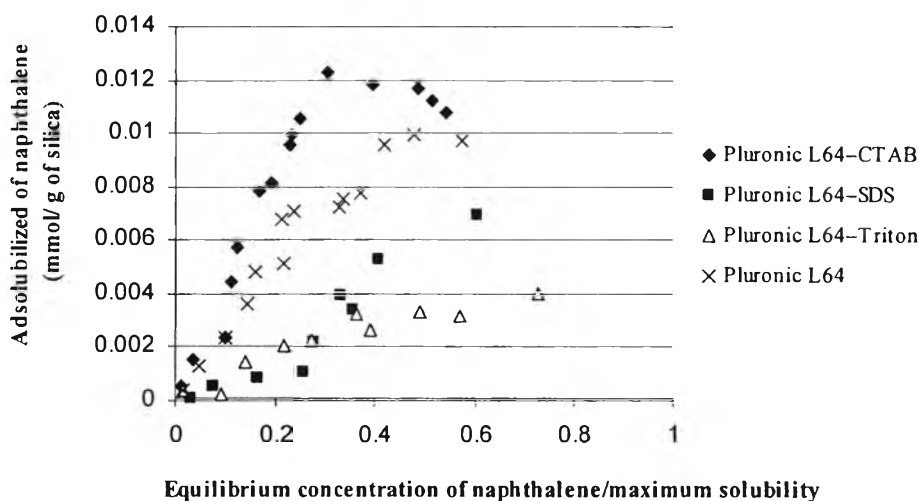


Figure 4.12 Adsolubilization of naphthalene in the different surfactant systems.

Increasing the equilibrium concentration of naphthalene for all systems can affect the increasing amount of adsolubilized of naphthalene. In the mixed surfactant system CTAB–Pluronic L64, the amount of adsolubilized naphthalene is the highest, whereas the lowest is observed in the mixed surfactant system Triton X-100–Pluronic L64. The results suggested that the adsolubilization of naphthalene may be related to the amount of adsorbed surfactant as the amount of adsorbed cationic surfactant–triblock copolymer; cetyltrimethyl ammonium bromide (CTAB)–Pluronic L64, is higher than the other systems.

From the above results it is possible to suggest that the amount of adsolubilized organic compound onto the hydrophilic silica depends on the amount of adsorbed surfactant onto the silica. Esumi *et al.* (2003) demonstrated that the adsolubilization of 2-naphthol does take place on the bare hydrophilic silica particles, whereas the adsolubilized organic capacity increases with the increase of adsorbed surfactant onto the silica. Several studies have suggested that the adsorption

mechanism changes for the different adsorption regions, which are thought to be due to the changes of the surface structure of the adsorbed aggregate surfactant.

The single surfactant system, block copolymer surfactant, Pluronic L64, has a higher adsolubilization capacity for organic solutes, especially those with small molecules or polar substances, than the other conventional surfactants. For the mixed surfactant system, cationic surfactant and block copolymer system (mixture A), has the highest organic adsorption capacity and when compare with a single block copolymer system, Pluronic L64, mixture A has higher adsolubilization amount (3.120 mmol of phenol/g of silica, 0.254 mmol of 2-Naphthol/g of silica, 0.023 mmol of naphthalene/g of silica) also higher than the single block copolymer, Pluronic L64, surfactant (2.410 mmol of phenol/g of silica, 0.195 mmol of 2-Naphthol/ g of silica, 0.017 mmol of naphthalene/g of silica).

Results from the study suggested that the adsolubilization of organic solutes may be related to the amount of adsorbed surfactant, as seen in the mixed system where the amount of adsorbed Pluronic L64 mixed with CTAB onto the silica surface is much higher than in the single Pluronic L64 system. The complex formation between the polymer and the conventional surfactant was due to the highly system-dependent nature of the interactions and electrostatic force. The synergism of CTAB mixed with Pluronic L64 on the hydrophobic particles may be stronger in a pure system than the hydrogen bonding between the PEO chains and the hydrophilic silica surface sites, as evidenced from the decreasing surface tension in the system controlled by the chemical structure of the cationic surfactant. At low surfactant adsorption, the structure, nature, or arrangement of the adsorbed CTAB on precipitated silica has a much stronger effect on the adsolubilization than the actual adsorbed amount. In addition, a cationic quaternary ammonium surfactant tends to adsorb onto an oppositely charged surface. The adsorption of CTAB onto the surface occurs initially via the electrostatic interaction between the cationic head groups and the anionic surface. However, the adsolubilization behaviors of the adsorbed CTAB aggregates in the different adsorption regions were quite distinct; suggesting that the structural arrangement of the surfactant aggregates may play an important part, in addition to the amount of adsorbed surfactant. This phenomenon was more

noticeable at low surfactant adsorption than at higher surface adsorption (Saphanuchart *et al.*, 2007).

For the mixed surfactant system between the anionic surfactant, SDS, and the block copolymer, Pluronic L64, (mixture B) it was found that adding the SDS to the block copolymer affects to the organic adsolubilization capacity. SDS in aqueous solutions involves important changes in the physio-chemical parameters of the block copolymer as a consequence of the strong interactions between the surfactants. The adsolubilized organic solute capacity of mixture B was lower than in the single Pluronic L64 system because there is repulsion between the ionic driving forces.

The association of SDS molecules with the block copolymer can affect the copolymer solution to become higher charge with increasing surfactant amount. The interaction between the block copolymer and the anionic surfactant changes the overall charge in the surfactant solution. Thus, the electrostatic repulsion from the same charge types between the headgroups of the SDS surfactant and the anionic charge on the absorbent surface, silica reduces the amount of surfactant adsorption compared to the single block copolymer Pluronic L64 system, which has no electrostatic repulsion.

The addition of the conventional surfactant into the Pluronic L64 solution resulted in increase and decrease in the amount of organic solutes captured on the silica particles, depending on the type of surfactant.

From the results, the nonionic surfactant–triblock copolymer, polyoxyethylene octyl phenol ether (Triton X-100)–Pluronic L64, system can adsolubilize the lowest amount of organic solutes, compared to the other mixed systems. This result suggested that when the surfactant concentration is increased, the apparent hydrodynamic radius (R_H) of the coil becomes progressively larger. It is suggested that the complex structure consists of clusters of micelles sited within the polymer coil. The synergism between Triton X-100 and Pluronic L64 makes this surfactant molecule change its form, making it difficult to be adsorbed onto the silica surface. Thus, the amount of surfactant adsorption in this mixed surfactant system might be less than expected. This is why only a small amount of each of three

organic solutes in this study can be adsolubilized into the Triton X-100–Pluronic L64 system.

Adsolubilization is strongly influenced by the amount of adsorbed surfactant, type of surfactant, ionic strength, and concentration. It is interesting to compare the adsolubilization amounts of phenol, 2-naphthol, and naphthalene that solubilized into the adsorbed surfactant layer of the mixed surfactant system. Besides the surfactant system, the properties of the organic solutes like polarity and structure of the organic solute such as size of molecule, number of aromatic ring also can affect the adsolubilization. The polarity of phenol and 2-naphthol is greater than naphthalene, which is a nonpolar solute. Thus, naphthalene is hard to adsolubilize into the surfactant, even in the mixed surfactant cationic and Pluronic L64 system. The result shows that the higher the polarity, the greater organic solute adsolubilization into the surfactant. Phenol and 2-Naphthol has hydroxyl as side group so they can be able to penetrate into both the palisade region and core region in adsorbed surfactant layer of the admicelle whereas naphthalene can be able to penetrate only the core region. Phenol has a high polarity, and also its molecule size is quite small. It can be adsolubilized easier into the admicelle surfactant, whereas 2-naphthol which has a longer molecule size can be adsolubilized than phenol even though it has a higher polarity. The naphthalene, which is nonpolar and is smaller than the 2-naphthol but larger than the phenol, has the lowest amount of adsolubilization of the three solutes. It is possible to propose that small molecules can more easily be adsolubilized and polar molecules strongly interact with the polar portions of the adsorbed block copolymers.