CHAPTER IV

RESULTS AND DISCUSSION

4.1 Adsorption of Surfactants onto Hydrophobic Silica

4.1.1 Adsorption Isotherms of Pluronic P123 with /without Linker Molecules

The adsorption isotherms of Pluronic P123 (PEO19PPO69PEO19, triblock copolymers) with and without linker molecules onto hydrophobic silica at 29 °C are shown in Figure 4.1. The results show that all of the adsorption isotherms of P123 are Langmuirian in shape (Rosen, 1989), and the maximum surfactant adsorption of P123 with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.096, 0.0981, 0.1 mmol of surfactant per gram of hydrophobic silica, respectively.

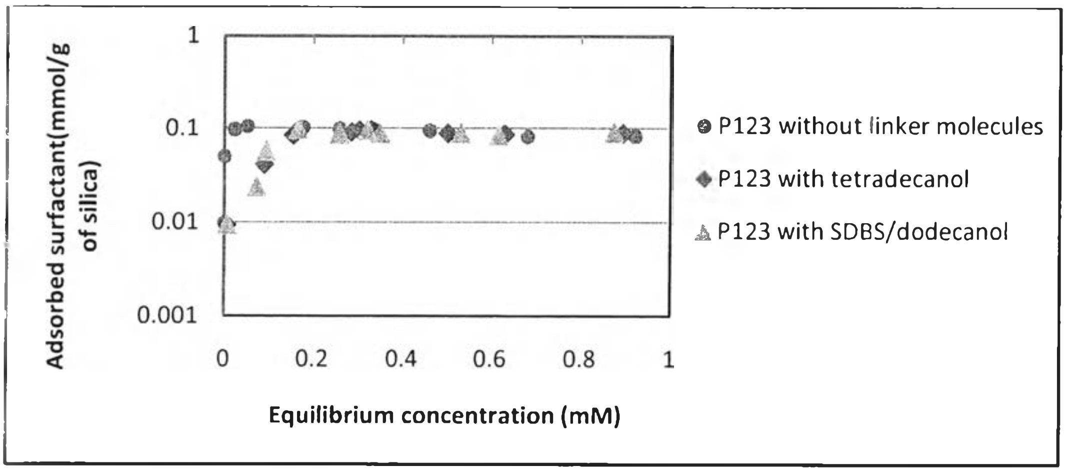

Figure 4.1 Adsorption isotherms of Pluronic P123 with /without linker molecules onto hydrophobic silica at 29 °C.

The adsorbed surfactant amounts of adsorption of P123 which use linker molecules are close to the system without linker molecules. This implies that linker molecules do not have significant effect on the adsorption of P123. This can be explained that P123 is the highest molecular weight surfactant of Pluronics family as their propylene oxide groups that adsorb onto hydrophobic silica surface are quite large. Therefore, they require a large area of hydrophobic silica surface to adsorb. In addition, there is relatively big gap between ethylene oxide groups of P123 so that when linker molecules were added to the system, the overall adsorption of P123 does not significantly change. This result indicates that linker molecules could not promote the surfactant tail-tail interactions (Tan and O'Haver, 2004).

4.1.2 Adsorption Isotherms of Pluronic L64 with /without Linker Molecules

The adsorption isotherms of Pluronic L64 ($PEO_{13}PPO_{30}PEO_{13}$, triblock copolymers) with and without linker molecules onto hydrophobic silica at 29 °C are shown in Figure 4.2. The results show that all of the adsorption isotherms of L64 are Langmuirian in shape (Rosen, 1989), and the maximum surfactant adsorption of L64 with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.0960, 0.0962, 0.095 mmol of surfactant per gram of hydrophobic silica, respectively.

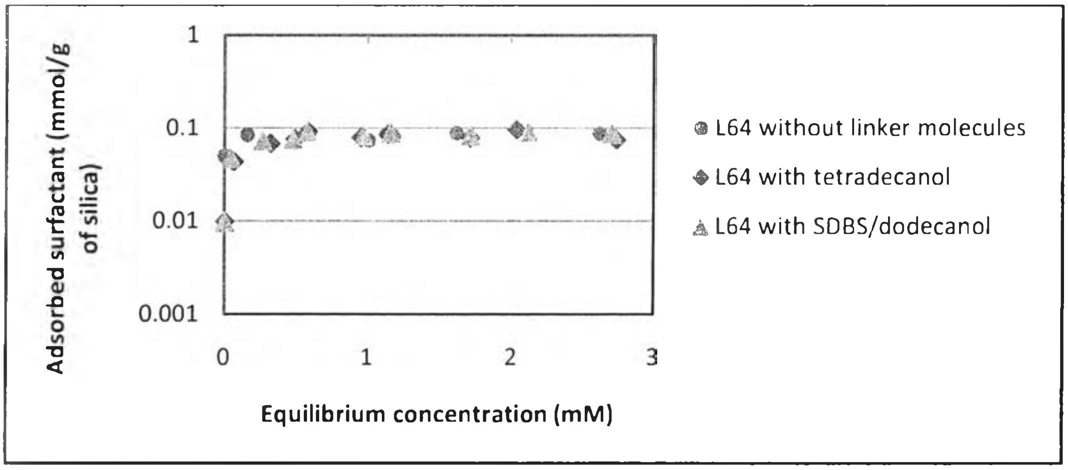

Figure 4.2 Adsorption isotherms of Pluronic L64 with /without linker molecules onto hydrophobic silica at 29 °C.

The adsorbed surfactant amounts of adsorption of L64 which use linker molecules are close to the system without linker molecules. This implies that linker molecules do not have significant effect on the adsorption of L64. This can be explained that L64 is a high molecular weight surfactant of Pluronics family as their propylene oxide groups that adsorb onto hydrophobic silica surface are very large. Therefore, they also require a large area of hydrophobic silica surface to adsorb. In addition, there is relatively big gap between ethylene oxide groups of L64 so that when linker molecules were added to the system, the overall adsorption of L64 does not significantly change. This result indicates that linker molecules could not promote the surfactant tail-tail interactions (Tan and O'Haver, 2004).

4.1.3 Adsorption Isotherms of Pluronic 25R4 with /without Linker Molecules

The adsorption isotherms of Pluronic 25R4 (PPO19PEO33PPO19, triblock copolymers) with and without linker molecules onto hydrophobic silica at 29 °C are shown in Figure 4.3. The results show that all of the adsorption isotherms of 25R4 are Langmuirian in shape (Rosen, 1989), and the maximum surfactant adsorption of 25R4 with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.064, 0.058, 0.041 mmol of surfactant per gram of hydrophobic silica, respectively.

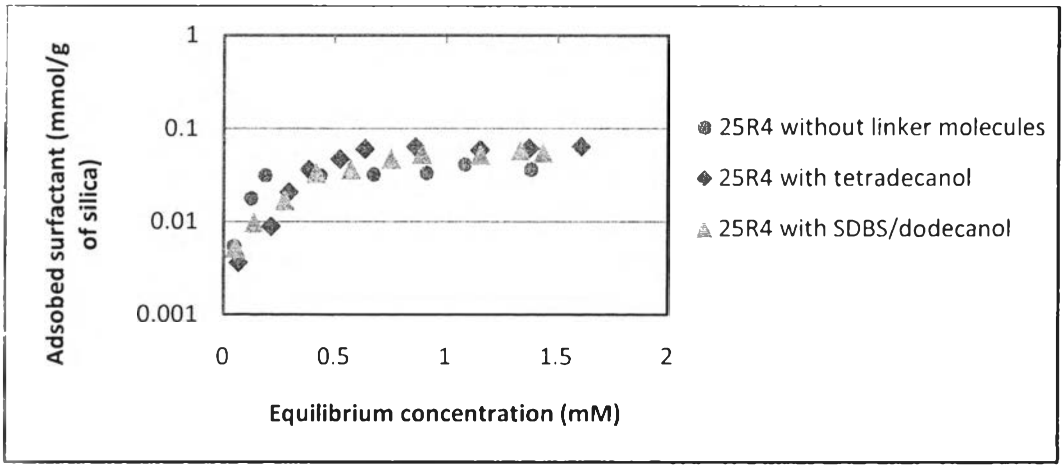

Figure 4.3 Adsorption isotherms of Pluronic 25R4 with /without linker molecules onto hydrophobic silica at 29 °C.

The adsorbed surfactant amounts of adsorption of 25R4 which use linker molecules are higher than the system without linker molecules. This implies that linker molecules have positive effect on the adsorption of 25R4. This can be explained that 25R4 is a reverse Pluronic. Thus, in this system, the shape of adsorbed of 25R4 onto hydrophobic silica surface looks like pancake shape. When linker molecules were added into the system, they could promote the hydrophobic region over the adsorbed surfactant layer. Ethylene oxide group which has higher hydrophobicity than propylene oxide group prefer to solubilize in that region rather than adsorb onto hydrophobic silica surface. Thus, 25R4 required less surface area to adsorb, leading to an increase in overall adsorpion of 25R4.

As can be seen in Figures 4.1-4.3, the adsorption isotherms of P123, L64, 25R4 are Langmuirian in shape (Rosen, 1989). P123 showed the highest adsorption onto hydrophobic silica, followed by L64, and 25R4, respectively. As P123 and L64 are normal pluronic, P123 had higher adsorbed amount than L64 due to stronger interaction between hydrophobic silica surface and propylene oxide groups (PO), "propylene oxide groups of P123 are larger than L64" (Tan and O'Haver, 2004). For 25R4, which is a reverse pluronic, it had the lowest adsorbed amount onto hydrophobic silica, indicating that the configuration of copolymers is an apparent factor for pluronic adsorption. From the previous work, Sahasyodhin (2010) found that configuration of Pluronic is an important factor for adsorption onto hydrophobic silica; normal Pluronics showed higher adsorption than reverse Pluronics.

4.2 Adsolubilization of Organic Compounds

Table 4.1 shows the amounts of adsorbed copolymer surfactants with/without linker molecules on hydrophobic silica that were used during the adsolubilization studies. We assume that the addition of the adsolubilizate in the system will not have significant effect the amount of adsorbed surfactant on the adsorbents.

Table 4.1 The amount of adsorbed copolymer surfactants on the adsorbents used in the adsolubilization studies

Copolymer surfactants	Adsorbed surfactant without linker molecules (mmol/g of silica)	Adsorbed surfactant with linker molecules (mmol/g of silica)
P123	0.09	0.080
L64	0.08	0.082
25R4	0.03	0.040

4.2.1 Adsolubilization of Phenol

4.2.1.1 Adsolubilization of Phenol into Adsorbed Pluronic P123 Layer

Figure 4.4 shows the adsolubilized amount of phenol into adsorbed pluronic P123 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of phenol into the adsorbed pluronic P123 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 14.546, 30.55, and 14.024 mmol/g of silica, respectively.

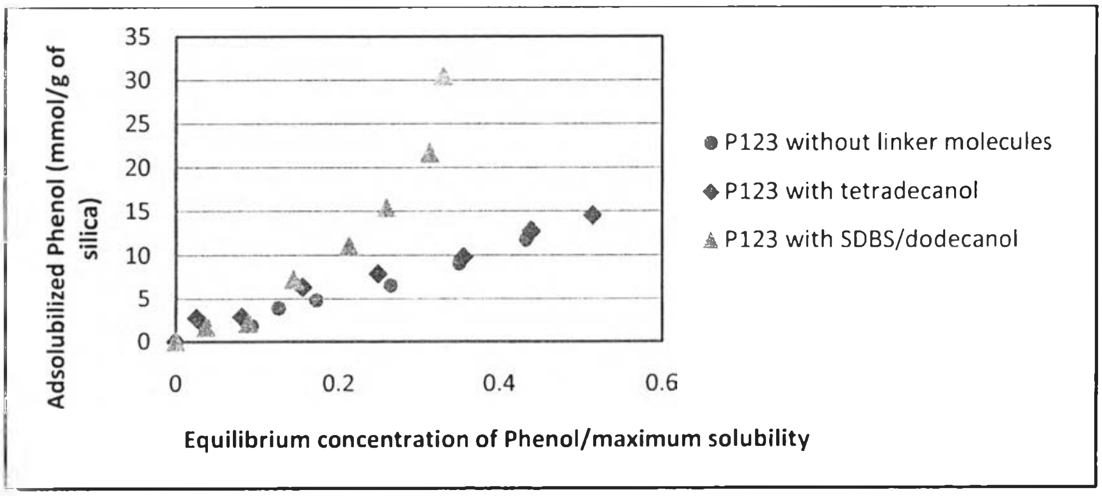

Figure 4.4 The adsolubilization of phenol into adsorbed P123 layer with /without linker molecules.

4.2.1.2 Adsolubilization of Phenol into Adsorbed Pluronic L64 Layer

Figure 4.5 shows the adsolubilized amount of phenol into adsorbed pluronic L64 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of phenol into the adsorbed pluronic L64 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 14.029, 20.93, and 12.61 mmol/g of silica, respectively.

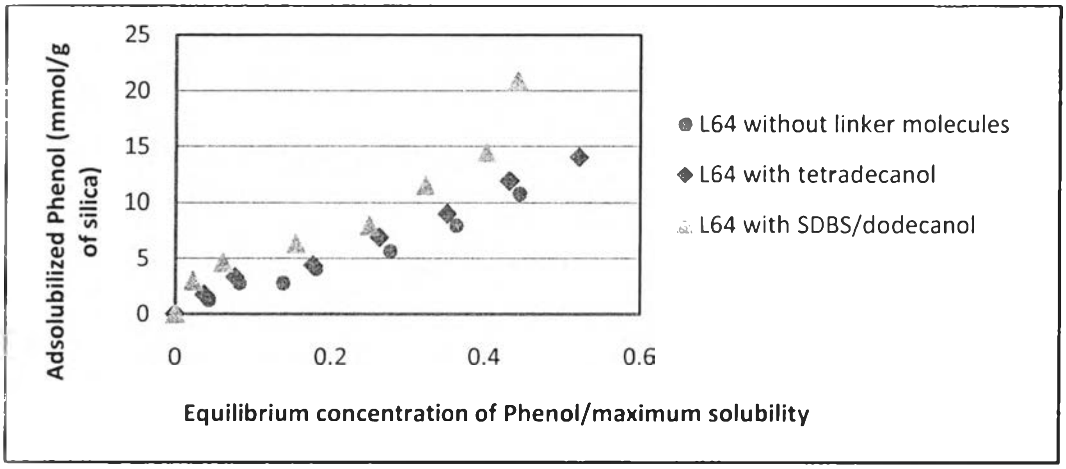

Figure 4.5 The adsolubilization of phenol into adsorbed L64 layer with /without linker molecules.

4.2.1.3 Adsolubilization of Phenol into Adsorbed Pluronic 25R4 Layer

Figure 4.6 shows the adsolubilized amount of phenol into adsorbed pluronic 25R4 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of phenol into the adsorbed pluronic 25R4 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS)

/dodecanol, and without linker molecules are 12.287, 17.187, and 7.88 mmol/g of silica, respectively.

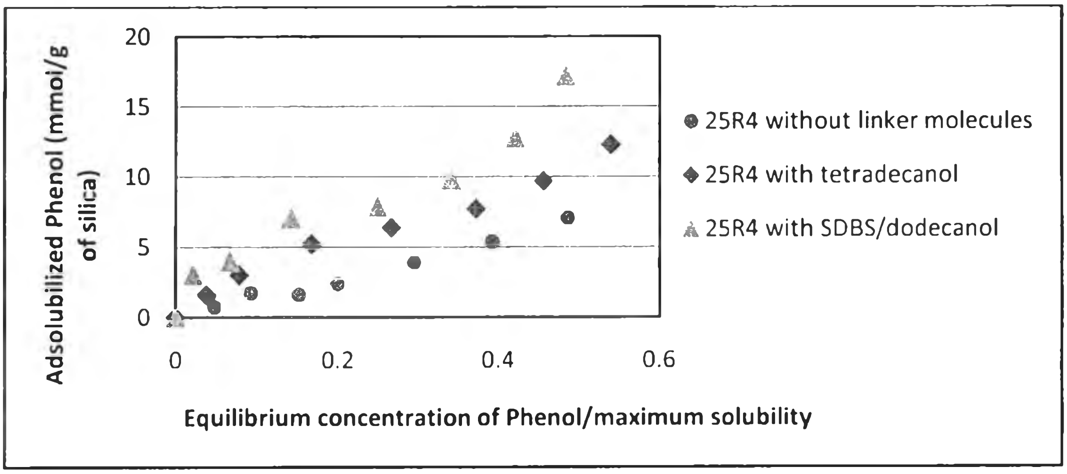

Figure 4.6 The adsolubilization of phenol into adsorbed 25R4 layer with /without linker molecules.

As can be seen in Figures 4.4-4.6, the adsolubilization of phenol in all systems increased with increasing bulk concentration. The system which used SDBS/dodecanol as linker molecules showed the highest adsolubilization of phenol followed by the system which used tetradecanol as linker molecules, and the system without linker molecules, respectively. For adsolubilization isotherms of phenol, it is interesting to see that all the adsolubilization isotherms of phenol with the combined linker system become nearly vertical at a bulk phenol concentration that is less than its solubility in water. Possible explanations can be offered the beginning of a phase separation inside the admicelle or the transition to a "two-dimensional microemulsion at the water–silica interface, increasing phenol concentration a new liquid phase or even droplets could begin to form in the core of the admicelle. These droplets would provide large reservoirs for the adsolubilization of additional phenol (Tan and O'Haver, 2004).

4.2.1.4 The Maximum Adsolubilization of Phenol into the Adsorbed Pluronics Layer

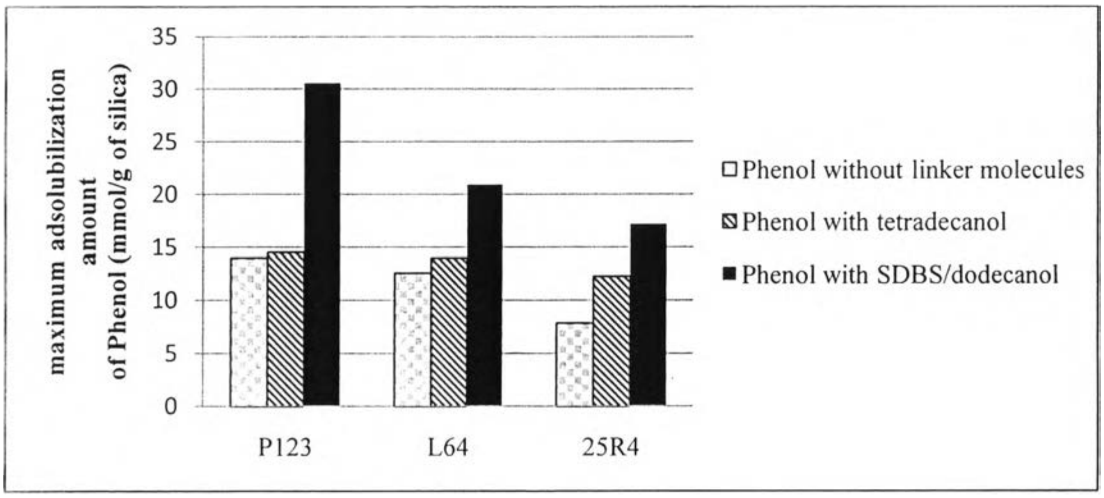

Figure 4.7 The maximum adsolubilization of phenol into the adsorbed surfactant layer of various types of pluronics with /without linker molecules at 29 °C.

Figure 4.7 shows the the maximum adsolubilization amounts of phenol into the adsorbed surfactant layer of various types of pluronics with/without linker molecules. All of the results showed that P123 had the highest adsolubilization followed by L64 and 25R4, respectively

4.2.2 Adsolubilization of 2-Naphthol

4.2.2.1 Adsolubilization of 2-Naphthol into Adsorbed Pluronic P123 Layer

Figure 4.8 shows the adsolubilized amount of 2-naphthol into adsorbed pluronic P123 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of 2-naphthol into the adsorbed pluronic P123 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.4636, 0.4863, and 0.4516 mmol/g of silica, respectively.

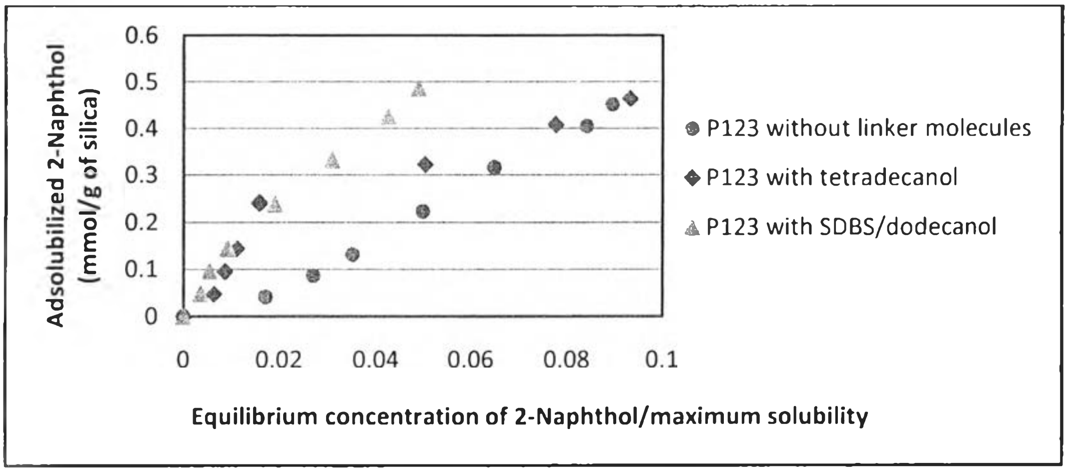

Figure 4.8 The adsolubilization of 2-naphthol into adsorbed P123 layer with /without linker molecules.

4.2.2.2 Adsolubilization of 2-Naphthol into Adsorbed Pluronic L64 Layer

Figure 4.9 shows the adsolubilized amount of 2-naphthol into adsorbed pluronic L64 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of 2-naphthol into the adsorbed pluronic L64 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.4304, 0.4792, and 0.4248 mmol/g of silica, respectively.

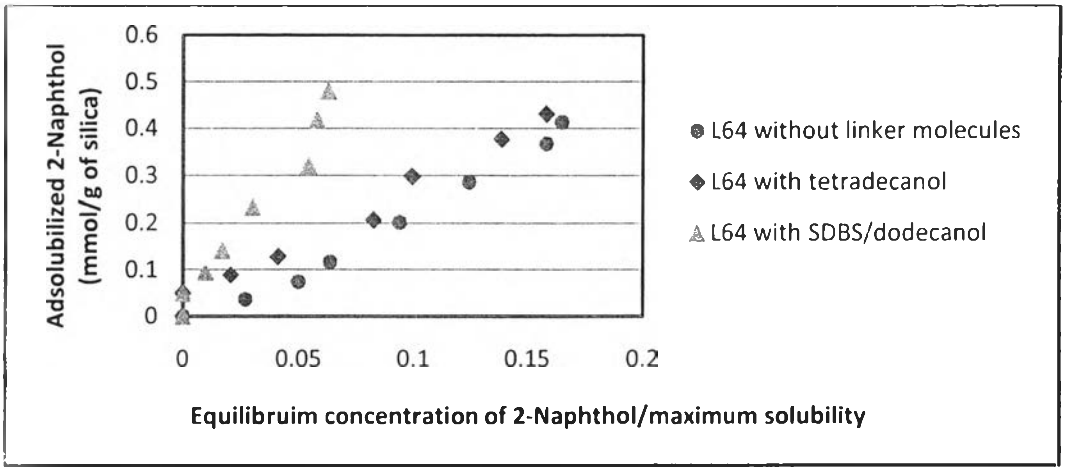

Figure 4.9 The adsolubilization of 2-naphthol into adsorbed L64 layer with /without linker molecules.

4.2.2.3 Adsolubilization of 2-Naphthol into Adsorbed Pluronic 25R4 Layer

Figure 4.10 shows the adsolubilized amount of 2-naphthol into adsorbed pluronic 25R4 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration/maximum solubility in water). The results show that the maximum adsolubilization amounts of 2-naphthol into the adsorbed pluronic 25R4 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.3827, 0.4277, and 0.34531 mmol /g of silica, respectively.

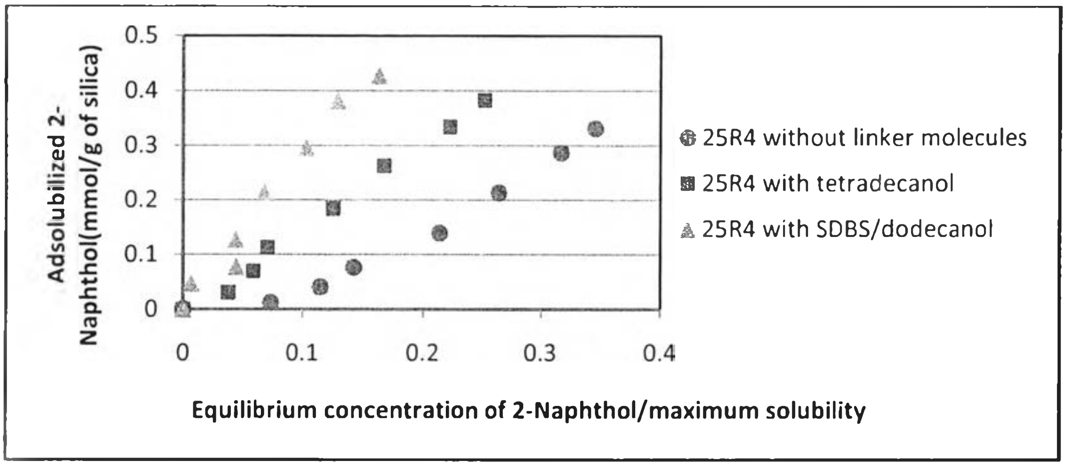

Figure 4.10 The adsolubilization of 2-naphthol into adsorbed 25R4 layer with /without linker molecules.

4.2.2.4 The Maximum Adsolubilization of 2-naphthol into the Adsorbed Pluronics Layer

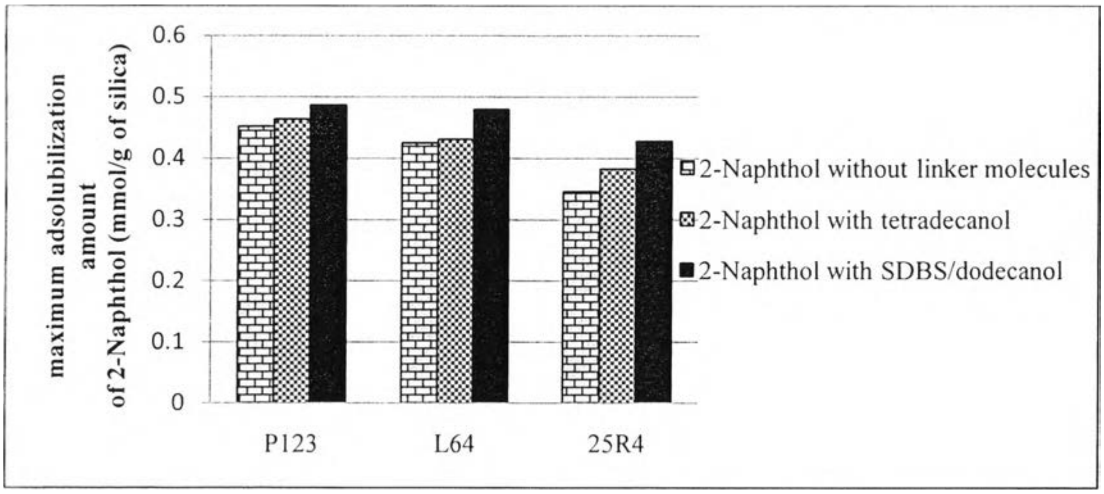

Figure 4.11 The maximum adsolubilization of 2-naphthol into the adsorbed surfactant layer of various types of pluronics with /without linker molecules at 29 °C.

Figure 4.11 shows the the maximum adsolubilization amounts of 2-naphthol into the adsorbed surfactant layer of various types of pluronics with /without linker molecules. All of the results showed that P123 had the highest adsolubilization followed by L64 and 25R4, respectively. Moreover, the system which used SDBS/dodecanol as linker molecules showed the highest adsolubilization followed by the system which used tetradecanol as linker molecules, and the system without linker molecules, respectively.

4.2.3 Adsolubilization of Naphthalene

4.2.3.1 Adsolubilization of Naphthalene into Adsorbed Pluronic P123 Layer

Figure 4.12 shows the adsolubilized amount of naphthalene into adsorbed pluronic P123 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of naphthalene into the adsorbed pluronic P123 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.0587, 0.15589, and 0.0534 mmol/g of silica, respectively.

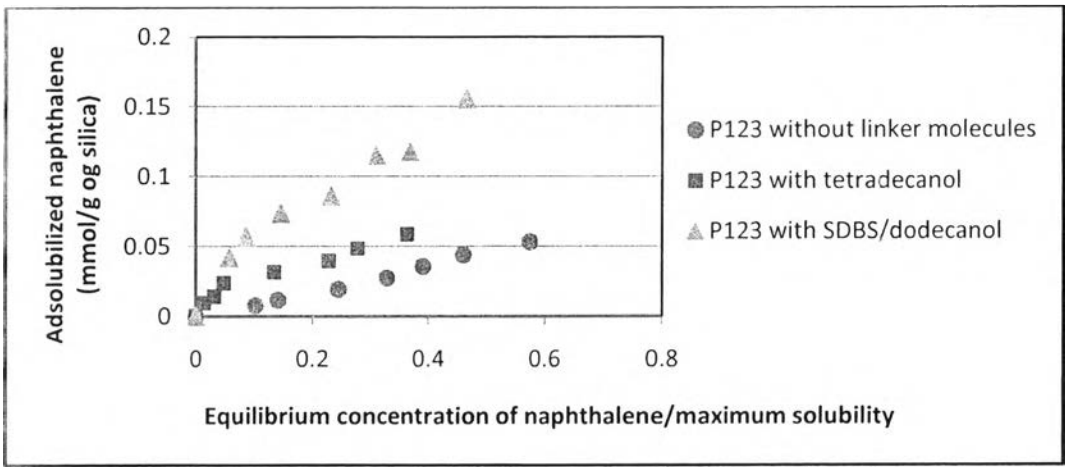

Figure 4.12 The adsolubilization of naphthalene into adsorbed P123 layer with /without linker molecules.

4.2.2.2 Adsolubilization of Naphthalene into Adsorbed Pluronic L64 Layer

Figure 4.13 shows the adsolubilized amount of naphthalene into adsorbed pluronic L64 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of naphthalene into the adsorbed pluronic L64 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules are 0.0554, 0.1430, and 0.0523 mmol/g of silica, respectively.

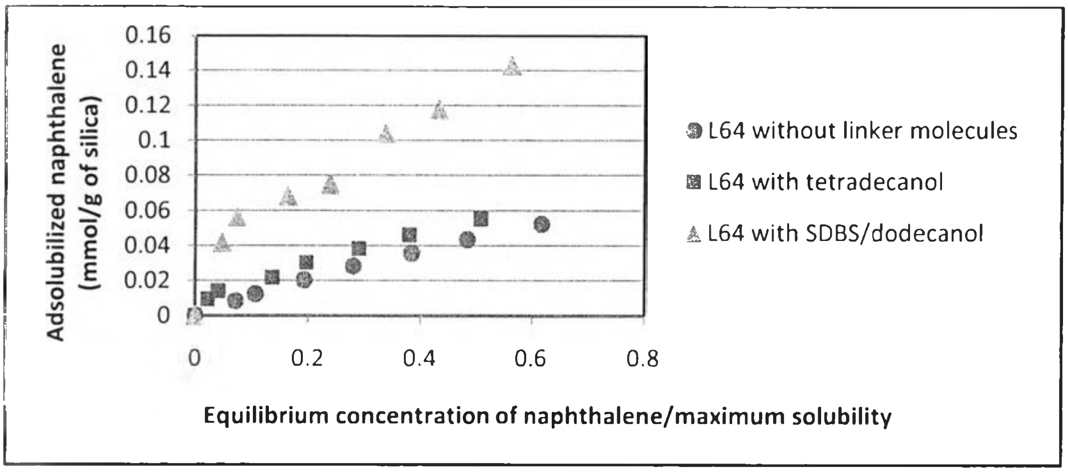

Figure 4.13 The adsolubilization of naphthalene into adsorbed L64 layer with /without linker molecules.

4.2.2.3 Adsolubilization of Naphthalene into Adsorbed Pluronic 25R4 Layer

Figure 4.14 shows the adsolubilized amount of naphthalene into adsorbed pluronic 25R4 layer with tetradecanol, with sodium dodecyl benzene sulfonate (SDBS) /dodecanol, and without linker molecules versus its reduced bulk concentration (equilibrium concentration /maximum solubility in water). The results show that the maximum adsolubilization amounts of naphthalene into the adsorbed pluronic 25R4 layer with tetradecanol, with sodium dodecyl benzene sulfonate

(SDBS) /dodecanol, and without linker molecules are 0.0309, 0.0973, and 0.028 mmol /g of silica, respectively.

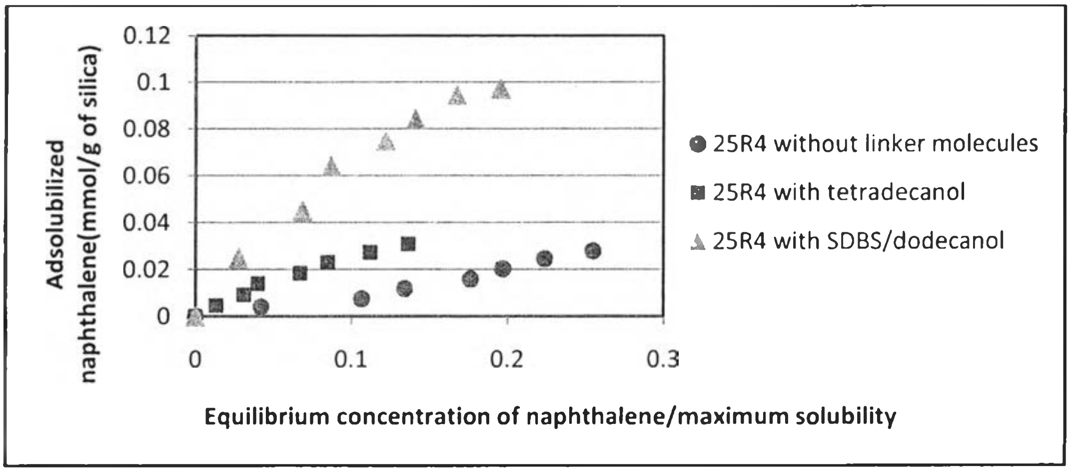

Figure 4.14 The adsolubilization of naphthalene into adsorbed 25R4 layer with /without linker molecules.

Figure 4.15 shows the the maximum adsolubilization amounts of naphthalene into the adsorbed surfactant layer of various types of pluronics with/without linker molecules. All of the results showed that P123 had the highest adsolubilization followed by L64 and 25R4, respectively. Moreover, the system which used SDBS /dodecanol as linker molecules showed the highest adsolubilization followed by the system which used tetradecanol as linker molecules, and the system without linker molecules, respectively.

4.2.2.4 The Maximum Adsolubilization of Naphthalene into the Adsorbed Pluronics Layer

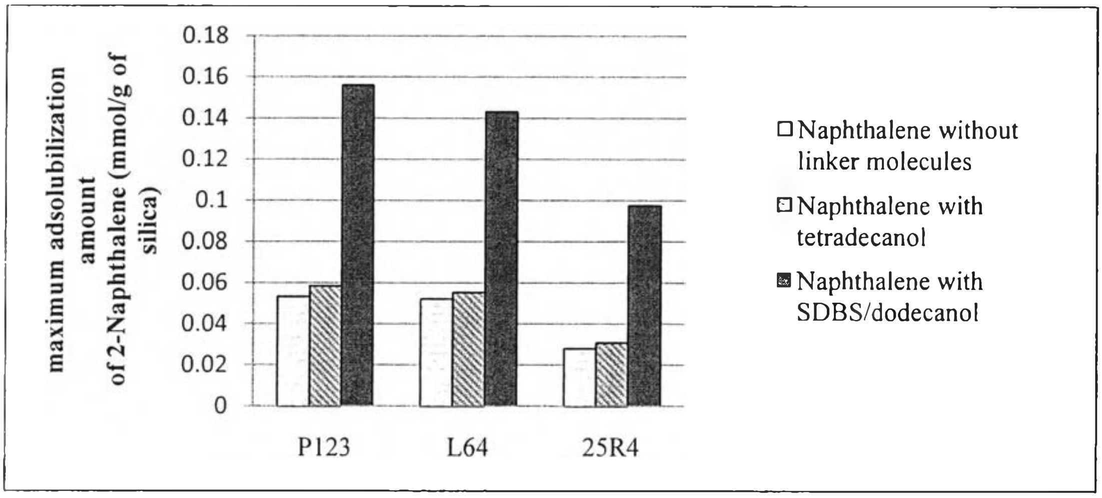

Figure 4.15 The maximum adsolubilization of naphthalene into the adsorbed surfactant layer of various types of pluronics with /without linker molecules at 29 °C.

For adsolubilization of phenol, 2-naphthol, and naphthalene as seen in the Figures 4.4-4.15. all of the results showed that P123 had the highest adsolubilization followed by L64 and 25R4, respectively. This can be explained that P123 is the highest molecular weight surfactant of Pluronics family; their propylene oxide groups that adsorb onto hydrophobic silica surface provide larger area for adsolubilization of organic compounds. In addition, there is relatively big gap between ethylene oxide groups of P123 in which organic compound preferentially adsolubilize (Tsurumi *et al.*, 2006). In contrast to 25R4, which is a reverse pluronic, the shape of adsorption of 25R4 onto hydrophobic silica looks like pancake shape, so there is no gap between ethylene oxide groups of 25R4.

The impact of linker molecules on adsolubilization of organic compounds is clearly seen when we refer back to the adsorption results. For adsorption studies, the adsorbed amount of pluronic has been shown to be quite similar in the system with and without linker molecules in contrast to adsolubilization studies. We expected that the presence of the linker molecules would promote hydrophobic interactions between surfactants tails and organic compounds in the admicelles and increase hydrophobicity of the adsorbed surfactant layer. As a result, the adsolubilization of organic compounds would be enhanced to a higher degree. From the adsolubilization results, increased adsolubilization amount was clearly observed in the systems having linker molecules. The combined linker system had shown to have the highest adsolubilization of organic compounds followed by lipophilic linker system, and the system without linker molecules, respectively. For these results, we will use a spherical or oblate ellipsoid surfactant aggregate structure to help explain, realizing that other types of aggregates may and probably do occur. In this structure, all the hydrophobic groups are in the center with hydrophilic groups, making up the surface of the aggregate. For a given aggregate size, surfactants with more EO groups will need more space, and thus, have fewer hydrophobic groups in the core region. Since linker molecules have a small hydrophilic group and a large hydrophobic tail, upon introduced into the system linker molecules will adsolubilize and increase the interactions between adjacent surfactant hydrophobic groups, promoting the formation of denser surfactant aggregates. Their presence increases the hydrophobicity of the aggregate core, which in turn promotes the adsolubilization of organic compounds (Tan and O'Haver, 2004). For combined linker system, it can be explained that when lipophilic and hydrophilic linker were added to the system, they formed a "self-assembled surfactant" at the surfactant tail and water interface. This could lead to an increase the water solubility of organic compounds and provide the hydrophobic region for adsolubilization of organic compounds (Sabatini *et al.*, 2003). For lipophilic linker system, it can be explained that the presence of tetradecanol can provide surfactant tail-tail interaction as well as increase hydrophobic region between surfactant tail which organic compounds preferentially adsolubilize into that region (Tsurumi *et al.*, 2006). As lipophilic linker molecules are less soluble in water than combined linker molecules, lipophilic linker system has lower adsolubilization of organic compounds than combined linker system.