CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorption of Surfactants onto Hydrophobic Silica

4.1.1 Adsorption Isotherm of Pluronic L31

The adsorption isotherm of Pluronic L31 ($PEO_1PPO_{17}PEO_1$, triblock copolymers, HLB 6.8) onto hydrophobic silica at 29°C is shown in Figure 4.1. The maximum surfactant adsorption occurs at the equilibrium concentration of 1.70 mM and the maximum adsorbed surfactant is 0.10 mmol of surfactant per gram of hydrophobic silica.

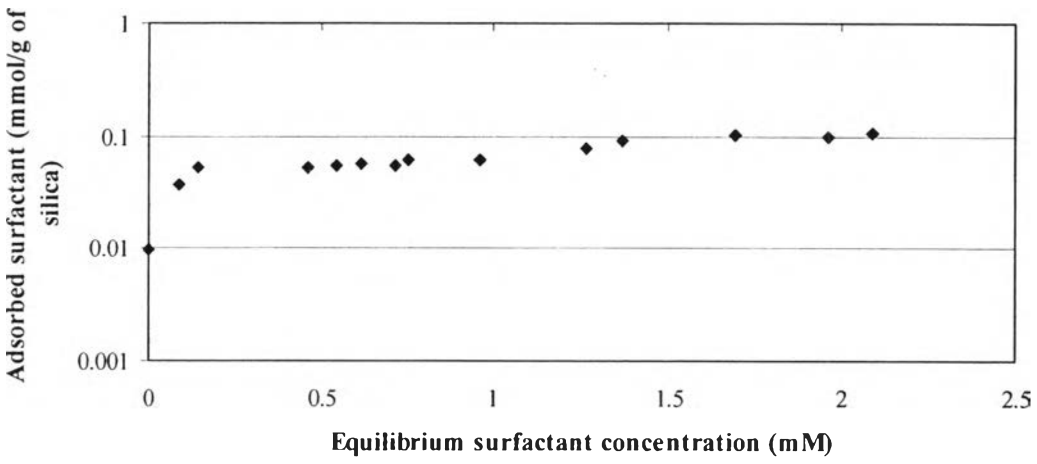

Figure 4.1 Adsorption isotherm of Pluronic L31 onto hydrophobic silica at 29°C (SD = ± 0.0012-0.0172).

The shape of L31 adsorption isotherm has two plateau regions. For the first plateau region, L31 is adsorbed parallel, or flat, on the hydrophobic surface increasing in coverage until it reaches monolayer saturation. The subsequent increase in adsorption is dominated by adsorbate-adsorbate interactions, where L31 is displaced from the surface by the adjacent molecules and changes to a more vertical orientation, resulting in a large increase in adsorption. This is due to the low number of EO groups in L31 (Paria and Khilar, 2004).

4.1.2 Adsorption Isotherm of Pluronic P123

The adsorption isotherm of Pluronic P123 ($PEO_{19}PPO_{69}PEO_{19}$, triblock copolymers, HLB 8) onto hydrophobic silica at 29°C is shown in Figure 4.2. The maximum surfactant adsorption occurs at the equilibrium concentration of 0.05 mM and the maximum adsorbed surfactant is 0.10 mmol of surfactant per gram of hydrophobic silica.

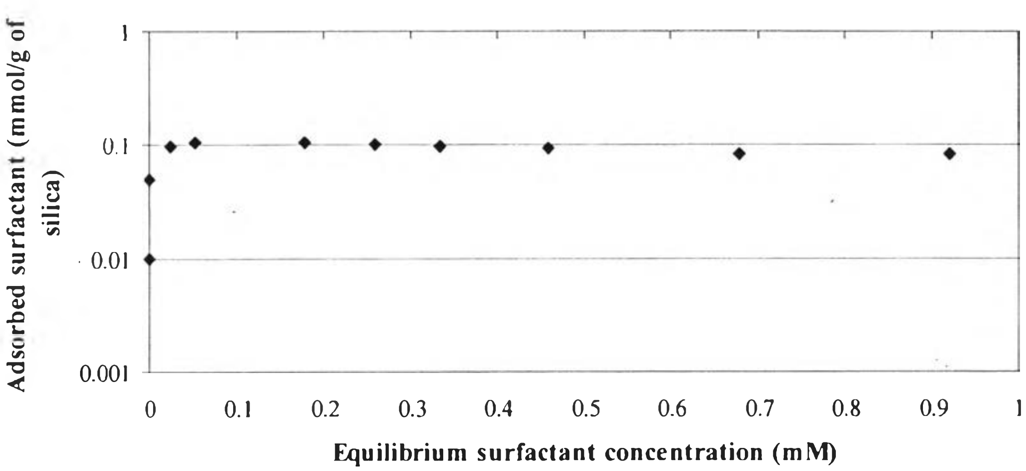

Figure 4.2 Adsorption isotherm of Pluronic P123 onto hydrophobic silica at 29°C (SD = ± 0.0011-0.0170).

4.1.3 Adsorption Isotherm of Pluronic L64

The adsorption isotherm of Pluronic L64 ($PEO_{13}PPO_{30}PEO_{13}$, triblock copolymers, HLB 15) onto hydrophobic silica at 29°C is shown in Figure 4.3. The maximum surfactant adsorption occurs at the equilibrium concentration of 0.16 mM and the maximum adsorbed surfactant is 0.08 mmol of surfactant per gram of hydrophobic silica.

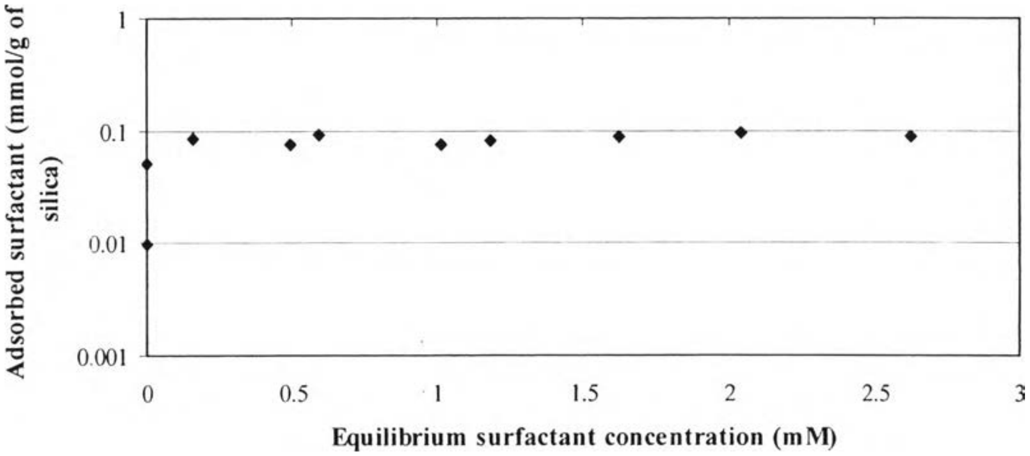

Figure 4.3 Adsorption isotherm of Pluronic L64 onto hydrophobic silica at 29°C (SD = ± 0.0012-0.0174).

4.1.4 Adsorption Isotherm of Pluronic 17R2

The adsorption isotherm of Pluronic 17R2 ($PPO_{15}PEO_{10}PPO_{15}$, reversed triblock copolymers, HLB 6) onto hydrophobic silica at 29°C is shown in Figure 4.4. The maximum surfactant adsorption occurs at the equilibrium concentration of 0.95 mM and the maximum adsorbed surfactant is 0.05 mmol of surfactant per gram of hydrophobic silica.

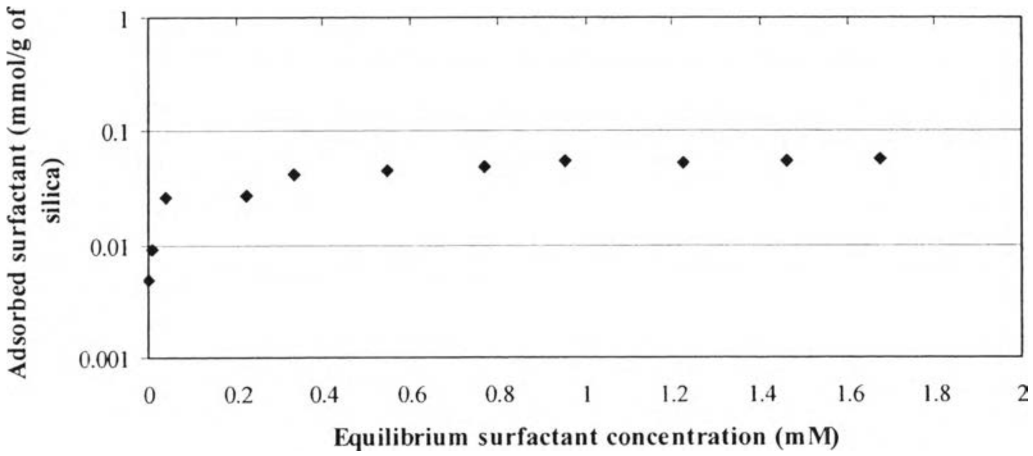

Figure 4.4 Adsorption isotherm of Pluronic 17R2 onto hydrophobic silica at 29°C (SD = ± 0.0008-0.0120).

4.1.5 Adsorption Isotherm of Pluronic 25R4

The adsorption isotherm of Pluronic 25R4 ($PPO_{19}PEO_{33}PPO_{19}$, reversed triblock copolymers, HLB 8) onto hydrophobic silica at 29°C is shown in Figure 4.5. The maximum surfactant adsorption occurs at the equilibrium concentration of 0.18 mM and the maximum adsorbed surfactant is 0.03 mmol of surfactant per gram of hydrophobic silica.

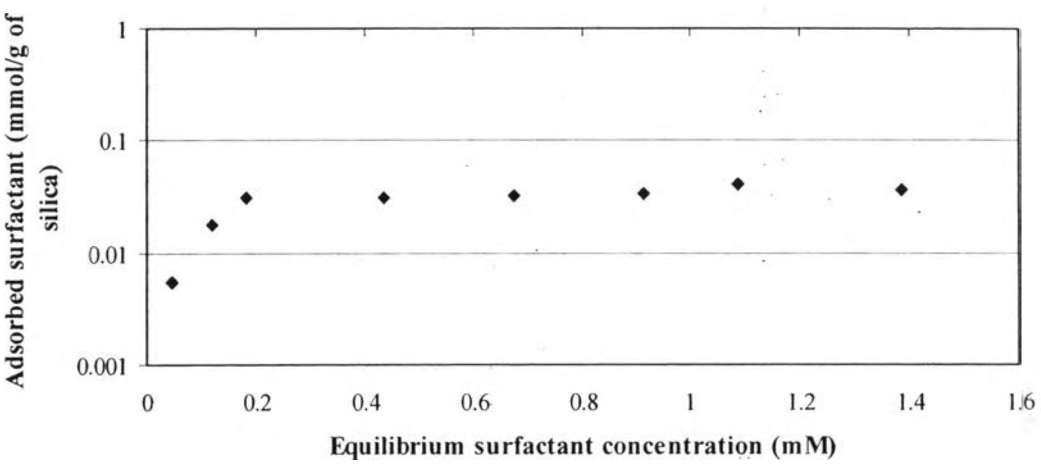

Figure 4.5 Adsorption isotherm of Pluronic 25R4 onto hydrophobic silica at 29°C (SD = ± 0.0009-0.0070).

4.1.6 Adsorption Isotherm of Pluronic 10R5

The adsorption isotherm of Pluronic 10R5 ($PPO_8PEO_{23}PPO_8$, reversed triblock copolymers, HLB 15) onto hydrophobic silica at 29°C is shown in Figure 4.6. The maximum surfactant adsorption occurs at the equilibrium concentration of 2.22 mM and the maximum adsorbed surfactant is 0.05 mmol of surfactant per gram of hydrophobic silica.

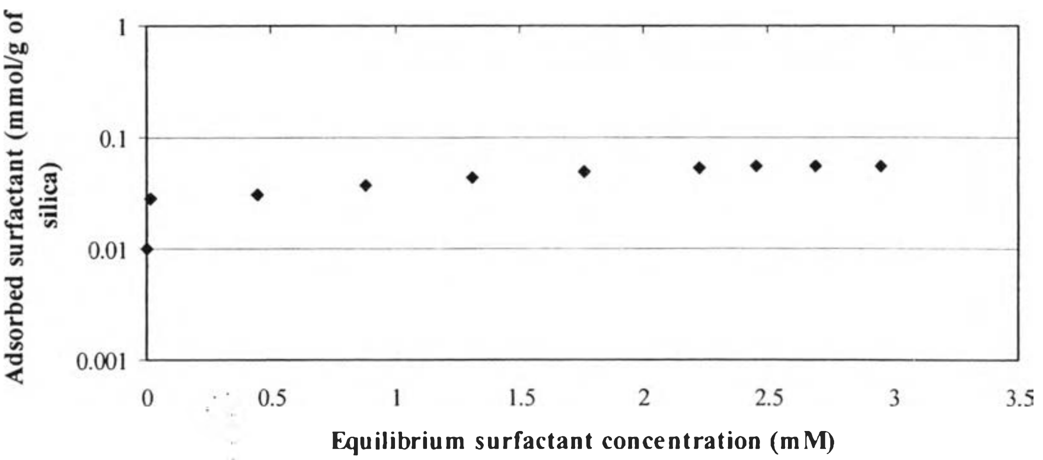

Figure 4.6 Adsorption isotherm of Pluronic 10R5 onto hydrophobic silica at 29°C (SD = ± 0.0010-0.0145).

Figure 4.7 shows the adsorption isotherms of various EO/PO triblock copolymers on hydrophobic silica surface.

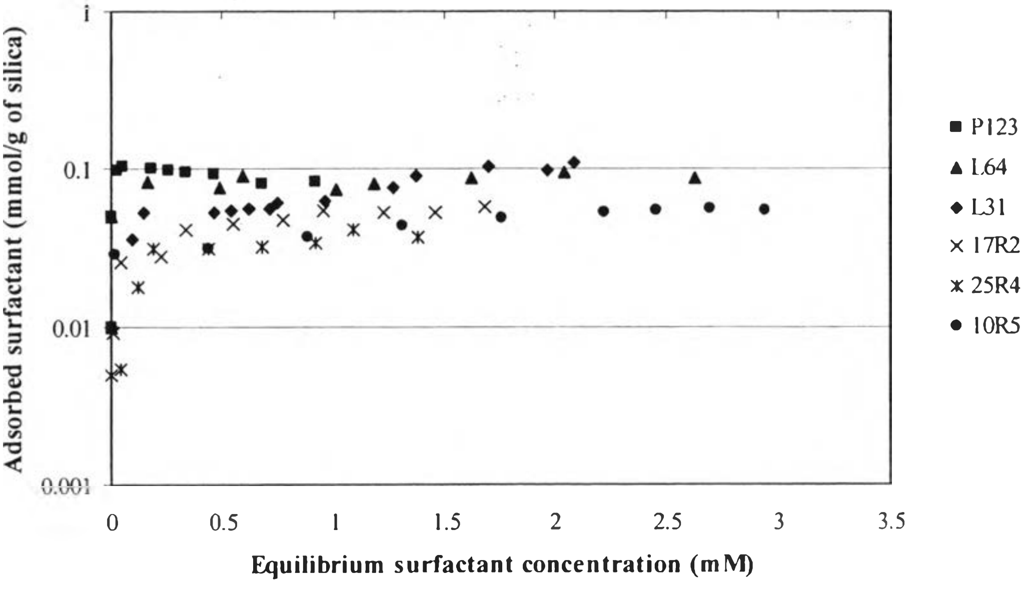

Figure 4.7 Adsorption isotherms of various copolymers on hydrophobic silica.

As can be seen in Figure 4.7, the adsorption isotherms of P123, L64, 17R2, 25R4, and 10R5 seem to be Langmuirian in shape (Rosen,1989). However, the shape of L31 adsorption isotherm is different from others, explain previously. P123 shows the highest adsorption onto hydrophobic silica, followed by L64, L31, 17R2, 25R4, and 10R5, respectively, it can be seen that Pluronics (L31, P123, L64) show higher adsorption than the reverse Pluronics (17R2, 25R4, 10R5), indicating that the configuration of copolymers is an apparent factor. Pluronics having lower HLB values and EO/PO ratio tend to show higher adsorption with the exception of L31. Lower HLB values and EO/PO ratio mean higher hydrophobicity which can interact highly with the hydrophobic surface. For L31, although it has lowest HLB value and EO/PO ratio, it shows lower adsorption than P123 and L64. The reason for this may be that L31 has much lower number of PO groups than P123 and L64 leading to a lower ability and probability of molecules to interact with the hydrophobic surface. Nevertheless, L31 shows highest maximum adsorbed amount due to the second step in adsorption, explain previously. The reverse Pluronics show the same trend as Pluronics where the ones with lower HLB values and EO/PO ratio tend to have higher adsorption.

The effect of configuration on adsorption is clearly seen when we compare the adsorption of Pluronic L64 and reverse Pluronic 17R2 which have the same number of PO units. L64 has a higher HLB values and EO/PO ratio and it would be expected to have lower adsorption, but the reverse is seen. We can conclude that configuration is an important factor for adsorption; Pluronics show higher adsorption than reverse Pluronics.

From the previous work, Wattanaphan (2008) found that L31 and 17R2 with HLB values lower than 7 did not appreciably adsorbed onto hydrophilic silica. For this work, L31 and 17R2 can adsorb onto hydrophobic silica due to the large number of PO groups that can interacting with the hydrophobic silica surface. In addition, Tsurumi *et al.* (2006) showed that Pluronics with HLB values higher than 18 did not adsorb well onto hydrophilic silica but it can adsorb well onto hydrophobic silica. Thus, hydrophobic silica is a better substrate for EO/PO triblock copolymers than hydrophilic silica because larger range of HLB values can be used.

4.2 Adsolubilization of Organic Compounds

4.2.1 Adsolubilization of Organic Compounds

Table 4.1 shows the amounts of adsorbed copolymer surfactants on hydrophobic silica that were used during the adsolubilization studies. We assume that the addition of the adsolubilizate in the system will not have significantly 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 (mmol/g of silica)
L31	0.05
P123	0.09
L64	0.08
17R2	0.02
25R4	0.03
10R5	0.05

4.2.1.1 Adsolubilization of Phenol

Figure 4.8 shows the amount of adsolubilized phenol versus its reduced bulk concentration (equilibrium concentration/maximum solubility in water). The results show that hydrophobic silica containing Pluronic P123 shows the highest adsolubilization, followed by hydrophobic silica containing L64, 10R5, 25R4, 17R2, and L31, respectively. From Table 4.1, hydrophobic silica containing P123 shows the highest adsorbed surfactant, followed by hydrophobic silica containing L64, 10R5 and L31, 25R4, and 17R2, respectively. Therefore, the order of adsolubilization is seem to be consistent with the order of amount of adsorbed surfactants on the surface of hydrophobic silica; higher amounts of adsorbed copolymer surfactant lead to higher levels of adsolubilization. This can be explained that higher amount of adsorbed surfactant provide a higher number of sites that is available to adsolubilize the molecules of phenol (Tsurumi *et al.*, 2006). For L31, although it has a moderate amount of adsorbed surfactant, it shows the lowest phenol adsolubilization. This is most likely because phenol molecules will adsolubilize into the EO region of the adsorbed copolymer surfactant layers (Schick, 1987). From the structure of L31, with its low number of EO units, this leads to a relatively low volume for phenol adsolubilization.

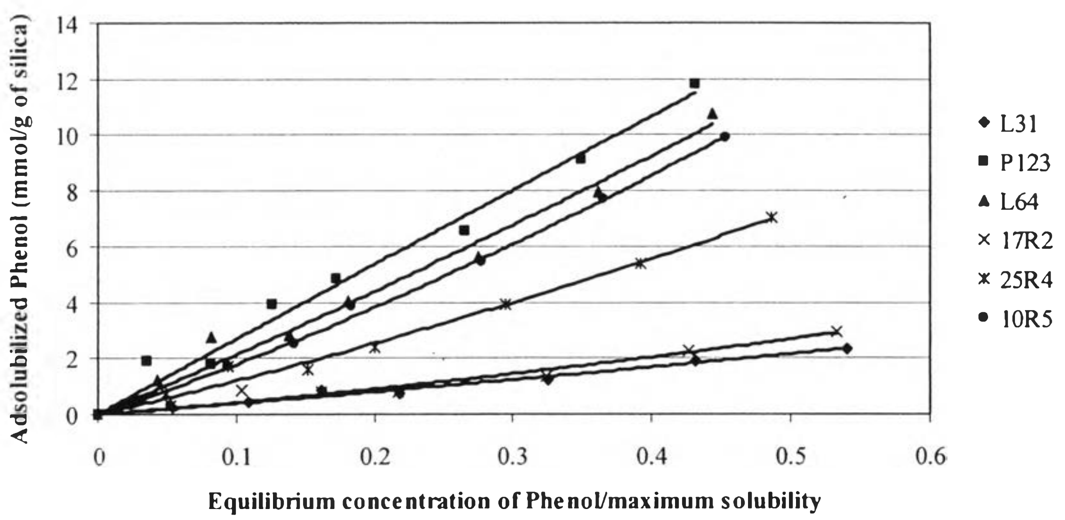

Figure 4.8 The adsolubilization of phenol in the examined surfactants (SD = ± 0.0900-0.2100).

In order to study the effect of the structure and properties of copolymers we may compare the adsolubilization of phenol into surfactants having the same amount of adsorbed surfactant. Figure 4.9 shows the adsolubilization ratio (adsolubilized phenol/adsorbed copolymer surfactants) versus its reduced bulk concentration. The results show that hydrophobic silica containing 25R4 has the highest adsolubilization, followed by hydrophobic silica containing 10R5, P123, L64, 17R2, and L31, respectively. Having high EO/PO ratio and high number of EO groups, 25R4 should provide a large volume for phenol partitioning and a high interaction with polar phenol, leading to highest adsolubilization. For 10R5, even though it has highest EO/PO ratio, but it has only a moderate number of EO groups.

For L64, P123, and 17R2, they have intermediate EO/PO ratios and also intermediate levels of adsolubilization. Having the lowest EO/PO ratio and lowest number of EO groups, L31 shows the lowest level of adsolubilization. Based on the results, the adsolubilization of phenol has shown to depend significantly on the EO/PO ratio and the number of EO groups of copolymers where copolymers with high EO/PO ratio and high number of EO groups show high adsolubilization. The reason that EO/PO ratio and number of EO groups affect the phenol adsolubilization can be explained that phenol is a polar organic molecule which tends to adsolubilize preferentially into highly polar regions, in this case, regions with high EO/PO ratio. Schick (1987) reported that phenol solubilized into the EO chain region of the micelles which implies that phenol molecules will probably be adsolubilized into the EO regions in admicelles. Therefore, high number of EO groups of copolymers provides favorable number of sites of the surfactant adsorbed layer for phenol molecules to adsolubilize.

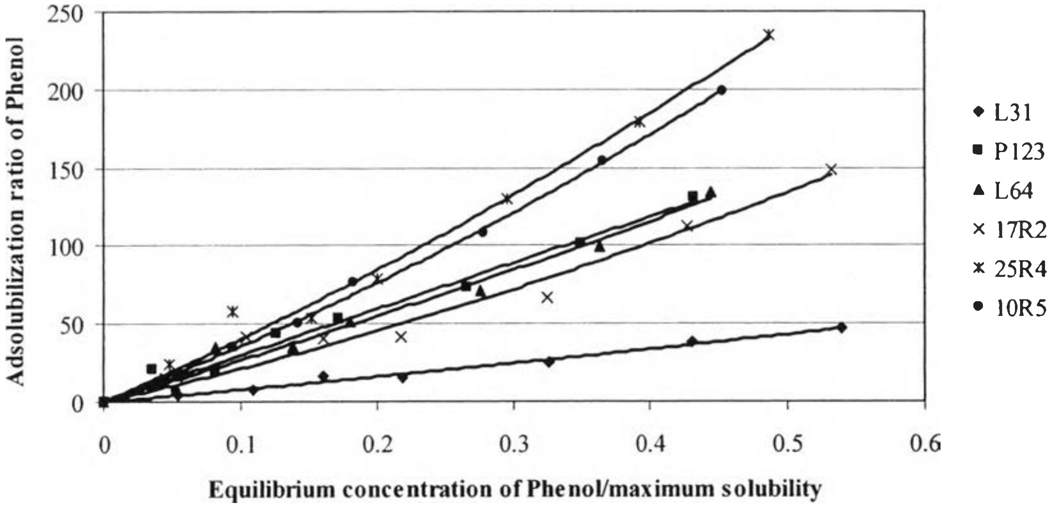

Figure 4.9 Adsolubilization ratio of phenol (SD = ± 1.0000-11.0000).

4.2.1.2 Adsolubilization of 2-Naphthol

Figure 4.10 shows the amount of adsolubilized 2-naphthol versus its reduced bulk concentration. It can be seen that hydrophobic silica with

P123 shows the highest adsolubilization, followed by hydrophobic silica with L64, 10R5, 25R4, 17R2, and L31, respectively. Similar to the adsolubilization of phenol, the order of 2-naphthol adsolubilization seems to be consistent with the order of adsorbed copolymer surfactants. Figure 4.11 shows the adsolubilization ratio versus its reduced bulk concentration. The degree of the adsolubilization seems to be enhanced as the number of EO blocks increases. Having higher number of EO groups, P123 and 25R4 show higher adsolubilization whereas L64, 17R2, and 10R5 have moderate number of EO groups show moderate in adsolubilization. Once again that L31 shows lowest adsolubilization because it has the lowest number of EO groups. Therefore, the important factor affecting 2-naphthol adsolubilization has shown to be the number of EO groups for the same reason as with phenol. Nevertheless, the EO/PO ratio does not seem to have much influence on 2-naphthol adsolubilization, which may be because the molecules of 2-naphthol are less polar than the phenol molecules.

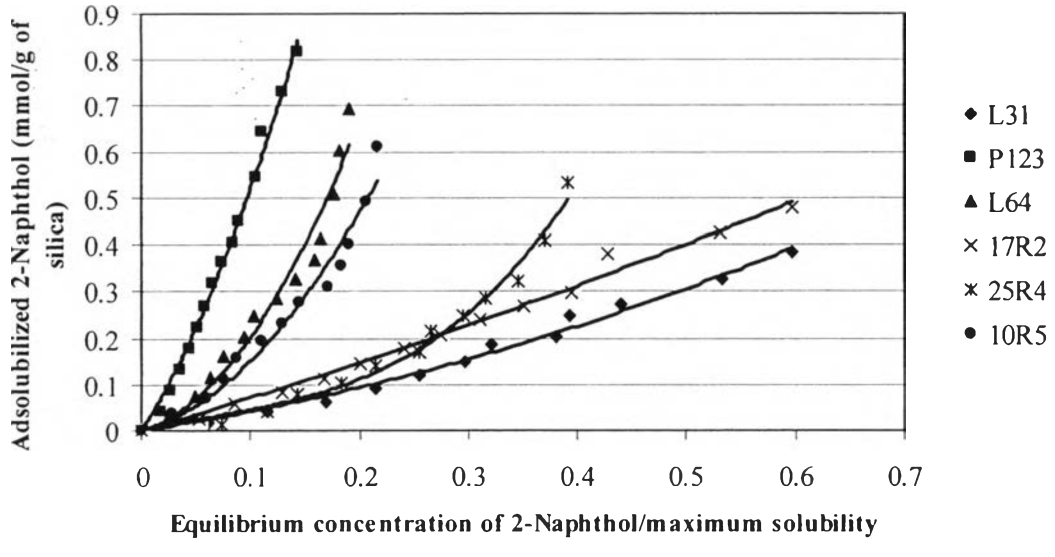

Figure 4.10 The adsolubilization of 2-naphthol in the examined surfactants (SD = ± 0.0020-0.0300).

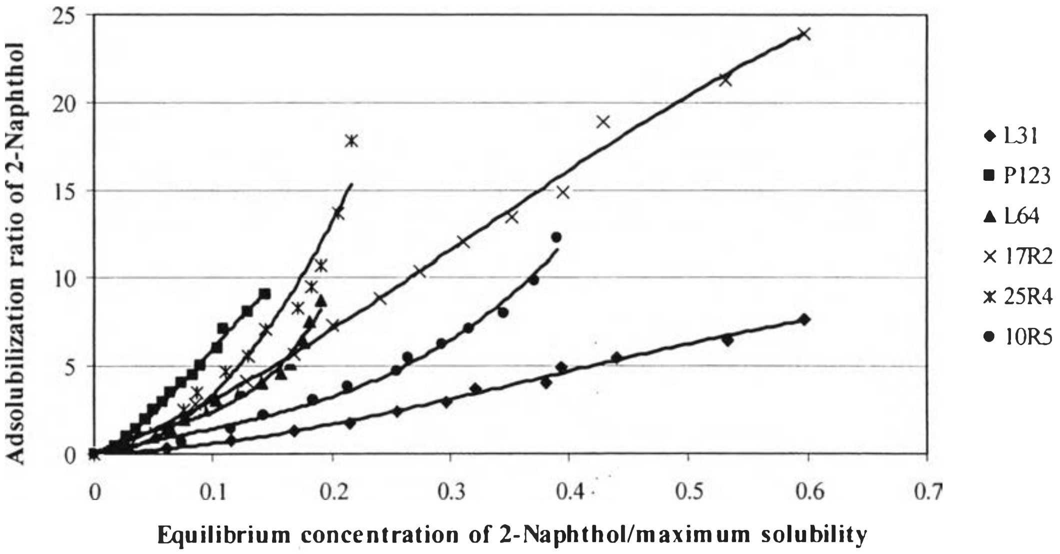

Figure 4.11 Adsolubilization ratio of 2-naphthol (SD = ± 0.1000-1.0000).

4.2.1.3 Adsolubilization of Naphthalene

Figure 4.12 shows the amount of adsolubilized naphthalene versus its reduced bulk concentration and Figure 4.13 shows the adsolubilization ratio versus its reduced bulk concentration. From Figure 4.12, although the amounts of adsorbed surfactants on hydrophobic silica used in the adsolubilization were different, the results show that the adsolubilization of naphthalene is almost the same for all copolymers studied, with an exception of L31. Comparing the ratio of adsolubilization to adsorbed surfactant (or the adsolubilization ratio), in Figure 4.13, the results show that the copolymers which have the lower amount of adsorbed surfactant show higher adsolubilization ratios, since all copolymers have approximately the same adsolubilization (Figure 4.12). For L31, the adsolubilization is different from others as it shows the lowest in adsolubilization both in Figure 4.12 and 4.13. The reason for this may be referred to Schick (1987) who explained that naphthalene would adsorb into the interface between the hydrophobic part and EO part of the surfactant adsorbed layer. In addition, L31 has very low number of EO groups leading to very low volume of interface to provide the sites for adsolubilization. Therefore, adsolubilization of naphthalene into L31 adsorbed layer has shown to be the lowest.

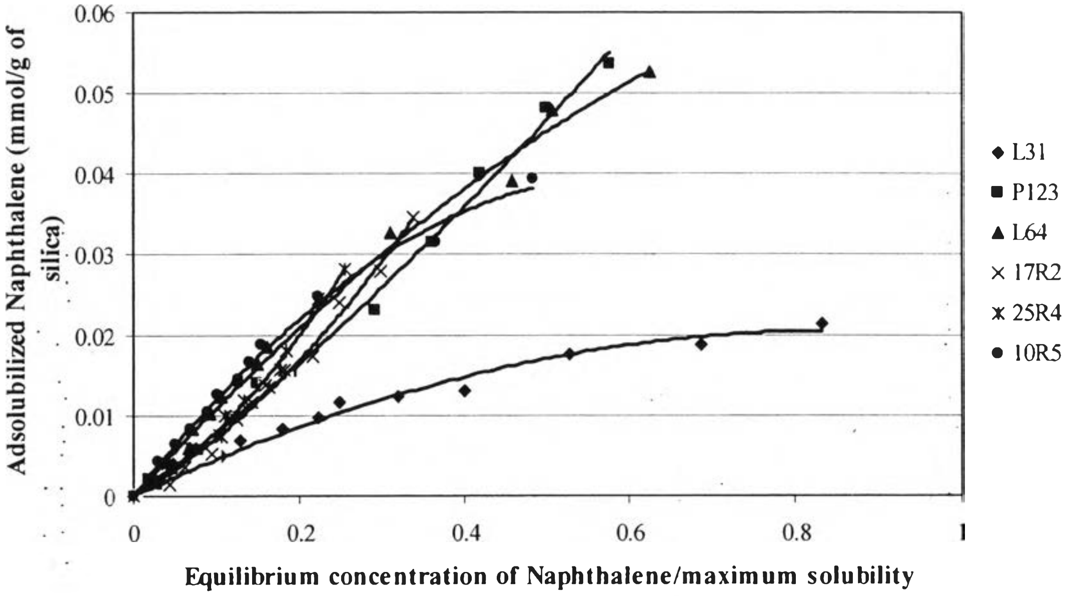

Figure 4.12 The adsolubilization of naphthalene in the examined surfactants (SD = ± 0.0008-0.0020).

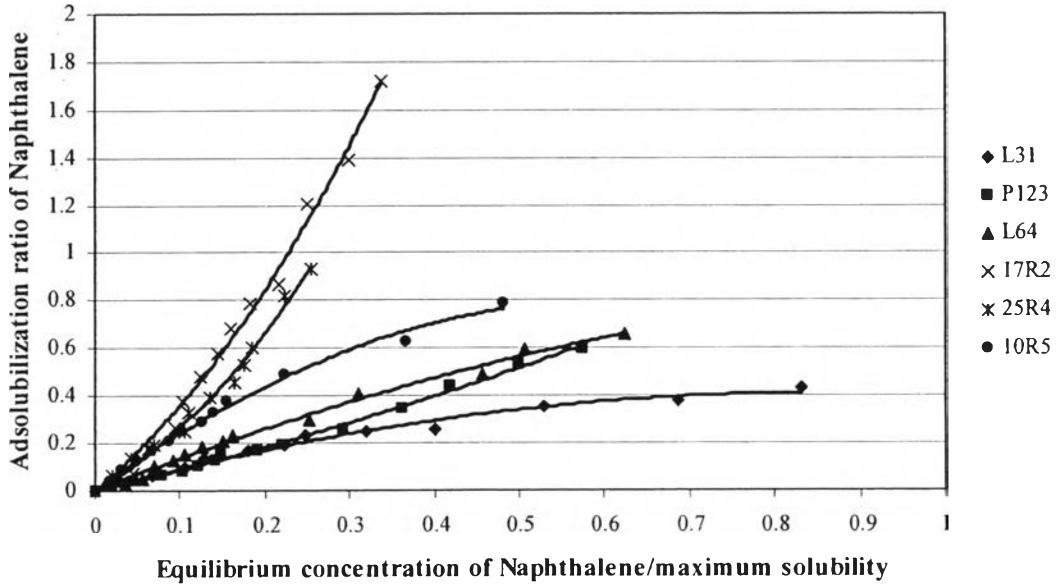

Figure 4.13 Adsolubilization ratio of naphthalene (SD = ± 0.0100-0.0600).

When we compare the adsolubilization result of this wok with our previous work (Wattanaphan, 2008), which used hydrophilic silica as an adsorbent, the adsolubilization of phenol, 2-naphthol, and naphthalene into the hydrophobic silica modified with EO/PO triblock copolymers (this work) is significantly higher than what observed previously when used hydrophilic silica. Therefore, it can be concluded that the model aromatic organic compounds can preferentially adsolubilize into the EO/PO triblock copolymers layer on hydrophobic silica to a higher degree than on the hydrophilic silica.

4.2.2 The Effects of The Structures of The Aromatic Organic Molecules to The Adsolubilization Behaviors

The adsolubilization of phenol, 2-naphthol, and naphthalene into the adsorbed layers of Pluronics L31, P123, L64, and reverse Pluronics 17R2, 25R4, 10R5 are shown in Figures 4.14, 4.15, 4.16, 4.17, 4.18, and 4.19, respectively.

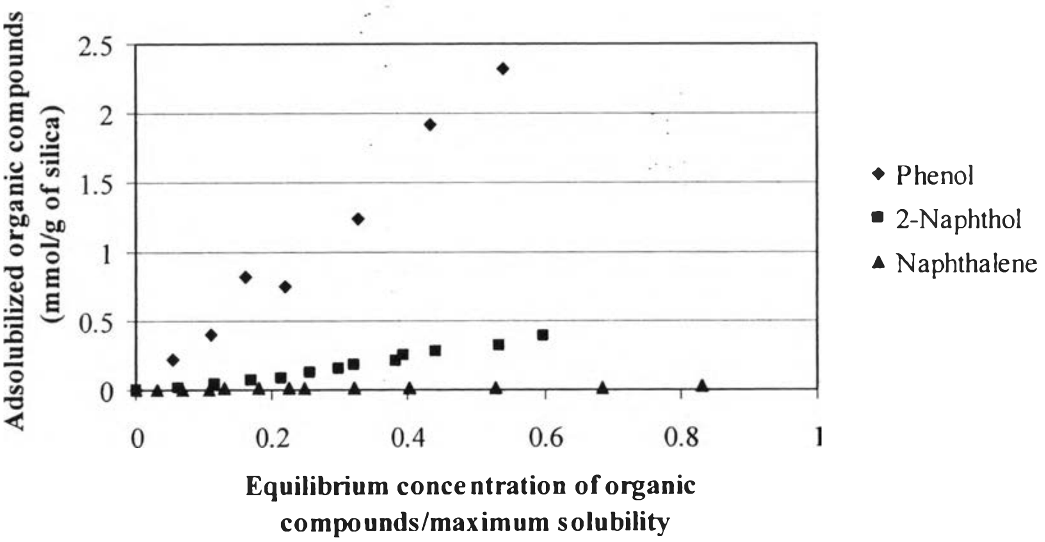

Figure 4.14 The adsolubilization of phenol, 2-naphthol, and naphthalene into the adsorbed layer of L31 on hydrophobic silica.

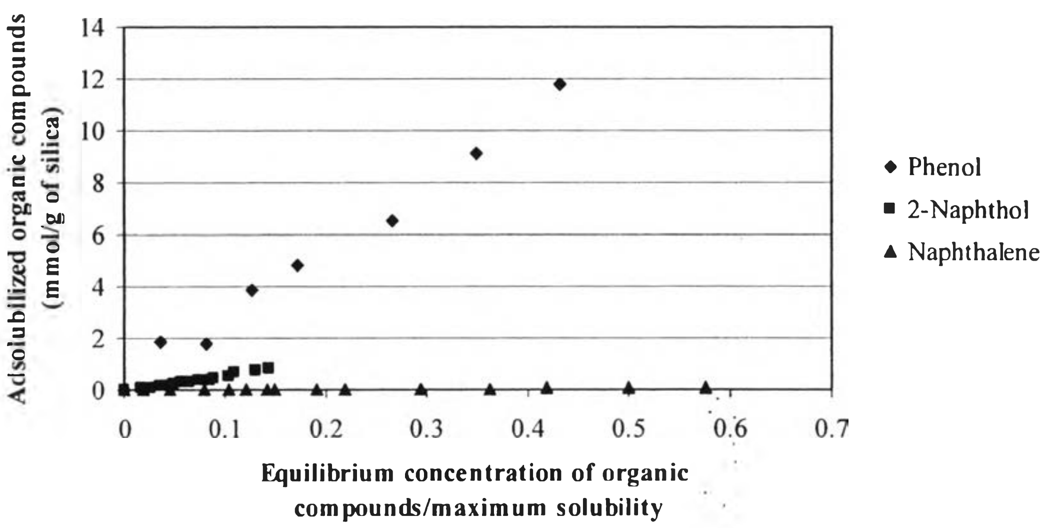

Figure 4.15 The adsolubilization of phenol, 2-naphthol, and naphthalene into the adsorbed layer of P123 on hydrophobic silica.

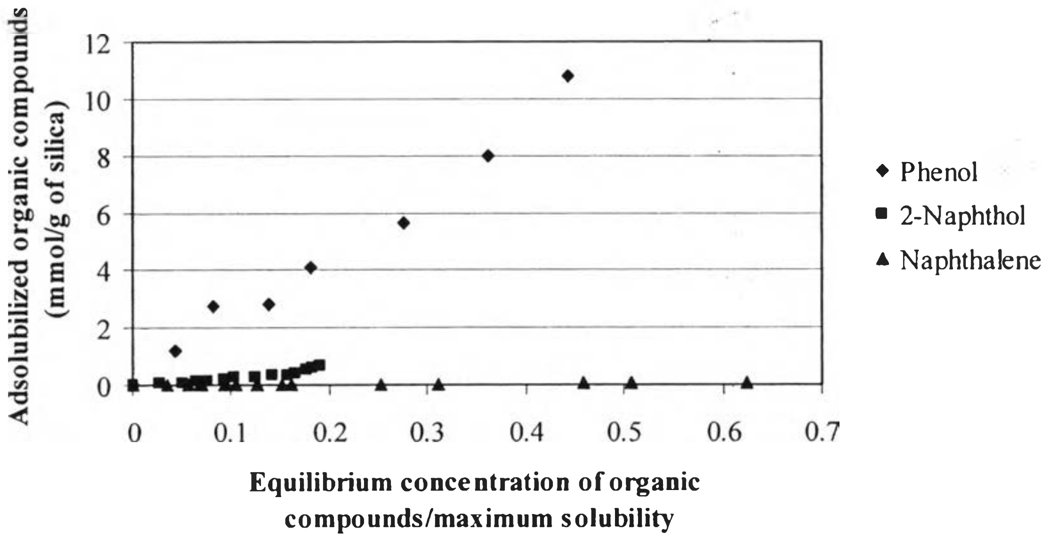

Figure 4.16 The adsolubilization of phenol, 2-naphthol, and naphthalene into the adsorbed layer of L64 on hydrophobic silica.

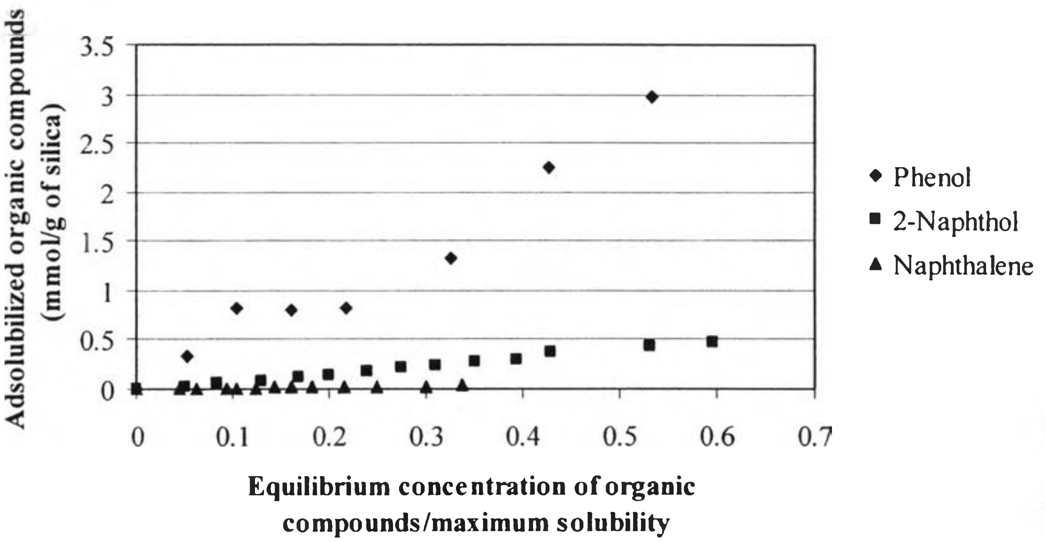

Figure 4.17 The adsolubilization of phenol, 2-naphthol, and naphthalene into the adsorbed layer of 17R2 on hydrophobic silica.

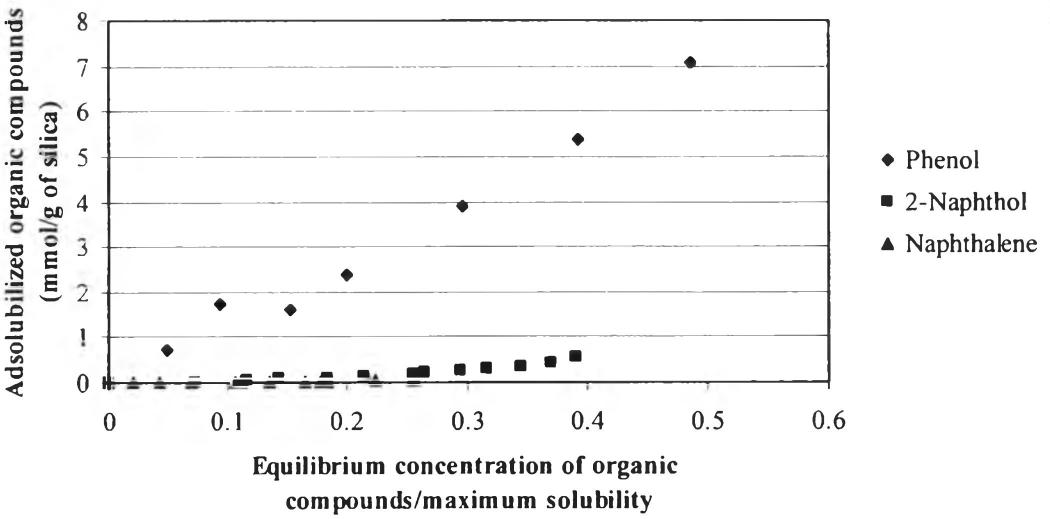

Figure 4.18 The adsolubilization of phenol, 2-naphthol, and naphthalene into the adsorbed layer of 25R4 on hydrophobic silica.

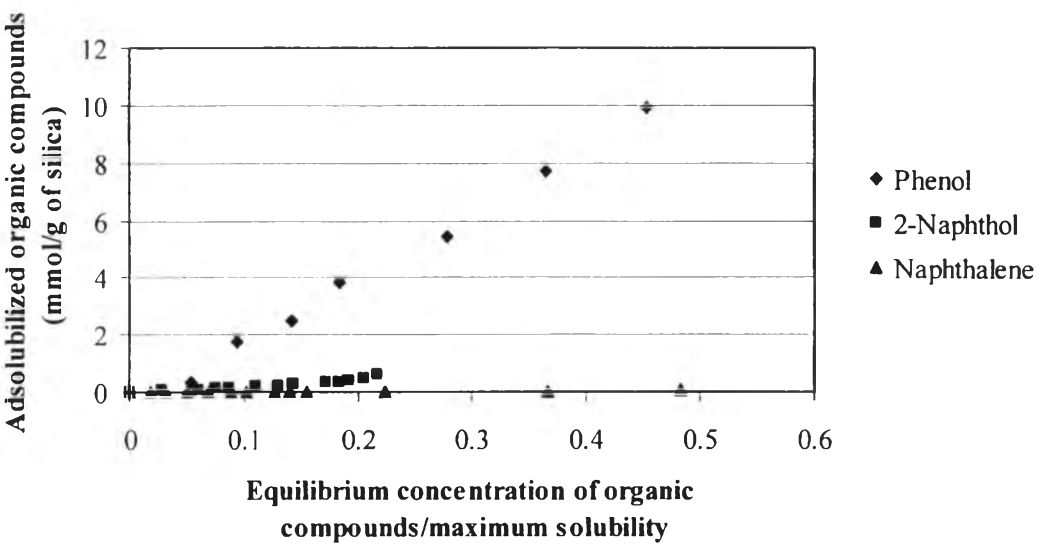

Figure 4.19 The adsolubilization of phenol, 2-naphthol, and naphthalene into the adsorbed layer of 10R5 on hydrophobic silica.

From Figures 4.14-4.19, the results show that adsolubilization of phenol is higher than 2-naphthol and naphthalene in all cases studied. This can be explained that phenol, which has a single benzene ring, is the smallest in size among the three compounds studied. The smaller molecule can easily penetrate and adsolubilize into the surfactant adsorbed layer and also take up less adsolubilization capacity. Therefore, due to the effect of the molecular size, smaller molecule can adsolubilize into surfactant adsorbed layer much higher than the larger ones.

Comparing the adsolubilization of 2-naphthol and naphthalene, 2-naphthol shows a higher degree of adsolubilization than naphthalene. This is because 2-naphthol has a hydroxyl group which makes it more polar, thus increasing the degree of interaction with the EO groups of the adsorbed layer. Naphthalene, which is polarizable, should adsolubilize primarily into the interface between the EO groups and hydrophobic parts (Schick, 1987). Therefore, for the systems studied, polar molecules adsolubilized to a greater extent than non-polar molecules.