



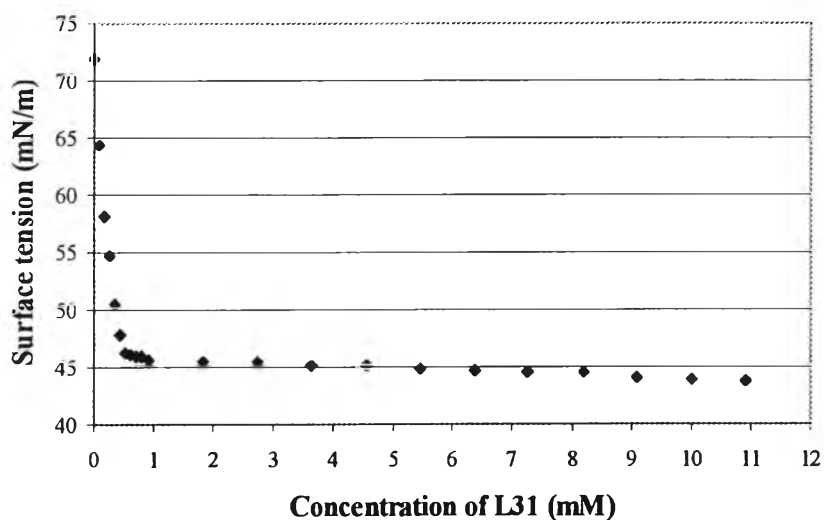
## CHAPTER IV

### RESULTS AND DISCUSSION

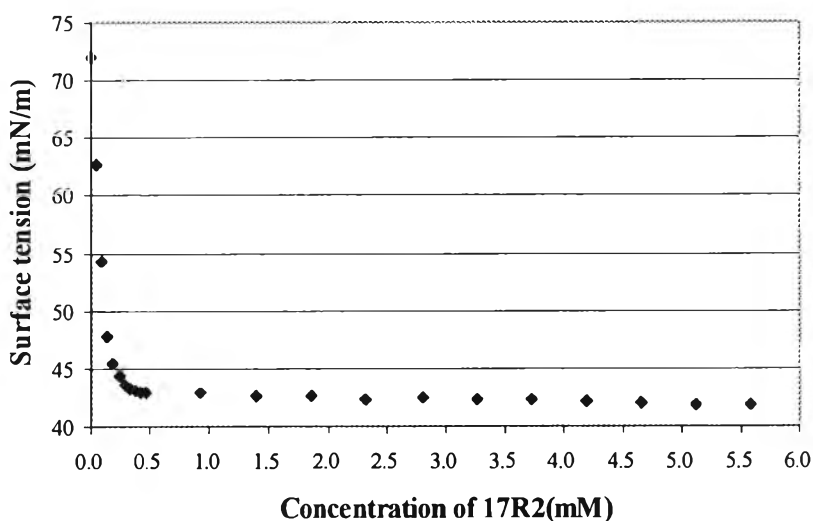
#### 4.1 CMC determination of surfactants

##### 4.1.1 CMC determination of surfactants in HLB range of 1-7

The surface tension versus concentration curves for Pluronic L31 (PEO<sub>1</sub>PPO<sub>17</sub>PEO<sub>1</sub>, triblock copolymers, HLB 6.8) and Pluronic 17R2 (PEO<sub>15</sub>PPO<sub>10</sub>PEO<sub>15</sub>, reversed triblock copolymers, HLB 6) at 29°C are shown in Figures 4.1 and 4.2, respectively. The results show that the CMC of L31 is approximately 0.45 mM and that of 17R2 is about 0.23 mM.



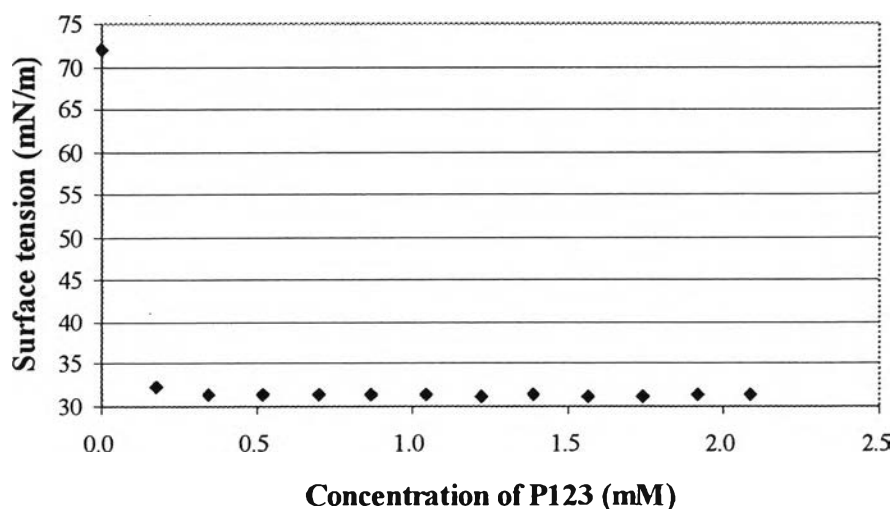
**Figure 4.1** Surface tension versus concentration curve for Pluronic L31.



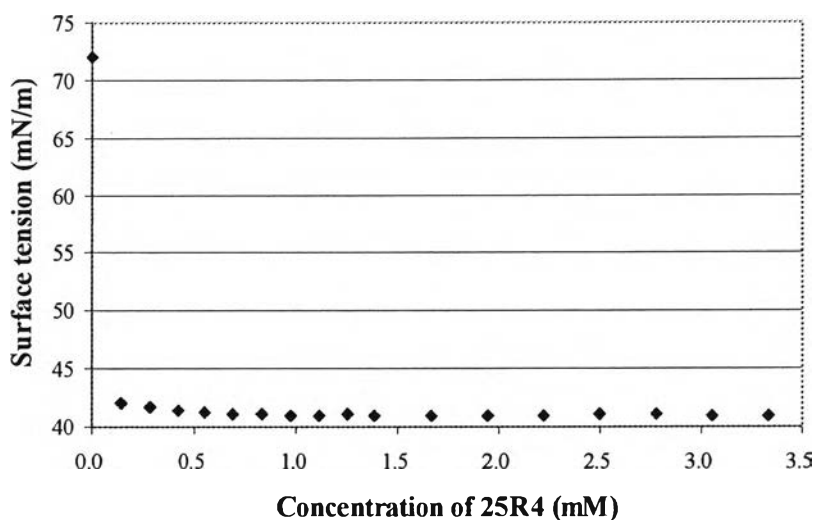
**Figure 4.2** Surface tension versus concentration curve for Pluronic 17R2.

#### 4.1.2 CMC determination of surfactants in HLB range of 7-12

The surface tension versus concentration curves of Pluronic P123 ( $\text{PEO}_{19}\text{PPO}_{69}\text{PEO}_{19}$ , triblock copolymers, HLB 8) and of Pluronic 25R4 ( $\text{PEO}_{19}\text{PPO}_{33}\text{PEO}_{19}$ , reversed triblock copolymers, HLB 8) at  $29^{\circ}\text{C}$  are shown in Figures 4.3 and 4.4, respectively. The results show that the CMC of P123 is approximately 0.35 mM, which roughly correlates to the literature value of 0.12 mM (Tsurumi *et al.*, (2006)). The CMC of 25R4 is approximately 0.69 mM.



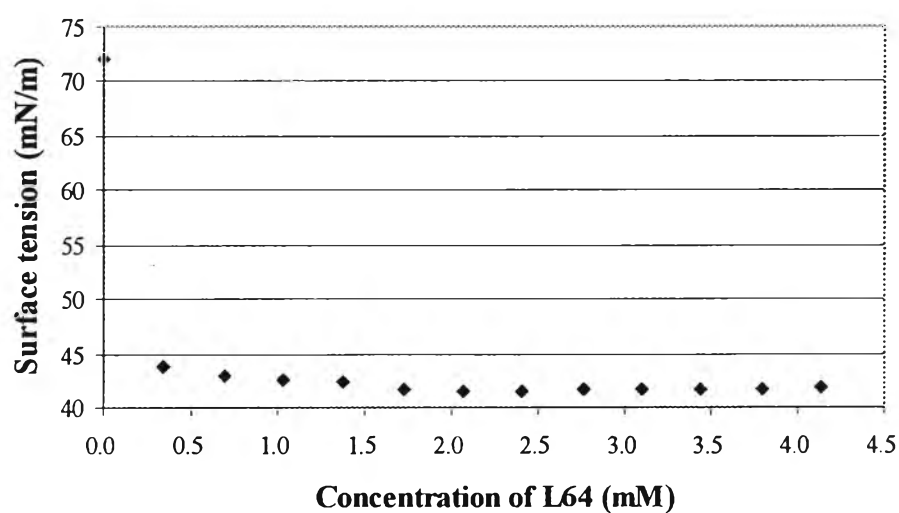
**Figure 4.3** Surface tension versus concentration curve for Pluronic P123.



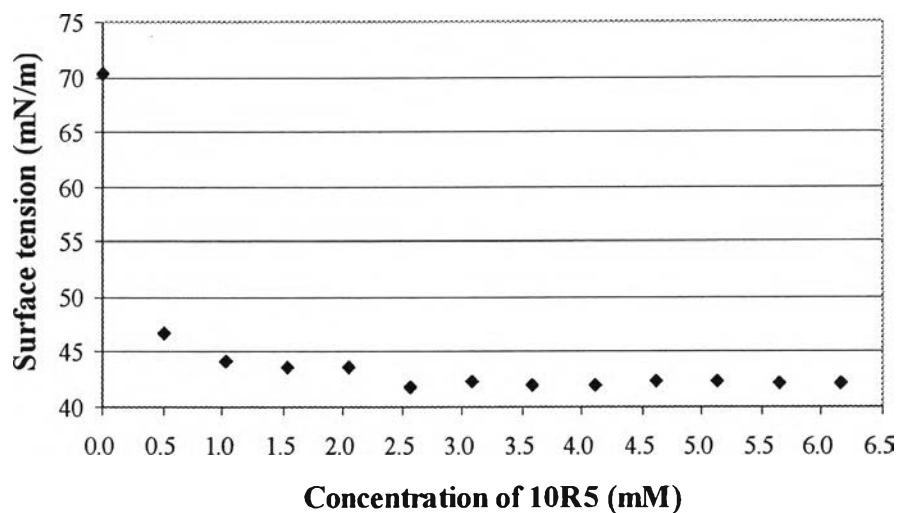
**Figure 4.4** Surface tension versus concentration curve for Pluronic 25R4.

#### 4.1.3 CMC determination of surfactants in HLB range of 12-18

The surface tension versus concentration curves for Pluronic L64 ( $\text{PEO}_{13}\text{PPO}_{30}\text{PEO}_{13}$ , triblock copolymers, HLB 15) and of Pluronic 10R5 ( $\text{PEO}_8\text{PPO}_{23}\text{PEO}_8$ , reversed triblock copolymers, HLB 15) at  $29^\circ\text{C}$  are shown in Figures 4.5 and 4.6, respectively. The CMC of L64 is approximately 1.72 mM, which correlates well with the literature value of 1.6 mM (Mata *et al.*, (2005)). The CMC of 10R5 is approximately 2.56 mM.

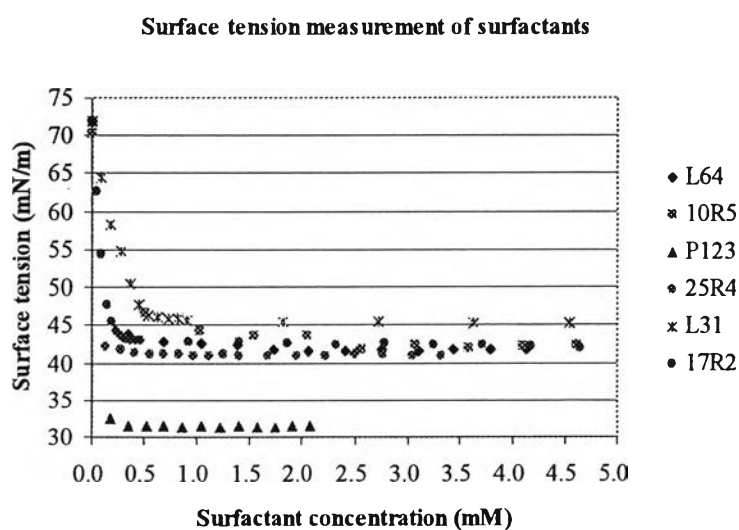


**Figure 4.5** Surface tension versus concentration curve for Pluronic L64.



**Figure 4.6** Surface tension versus concentration curve for Pluronic 10R5.

Therefore, the CMC of Pluronic L31, 17R2, P123, 25R4, L64, and 10R5 appear to be about 0.45, 0.23, 0.35, 0.69, 1.72, and 2.56 mM, respectively as shown in Figure 4.7. The factors that contribute to CMC are their HLB values and PO molecular weight. As the results shown for the same HLB values, the higher PO molecular weight tends to have a lower CMC. The influence of EO/PO ratio is less pronounced than that of the PO molecular weight in this case.

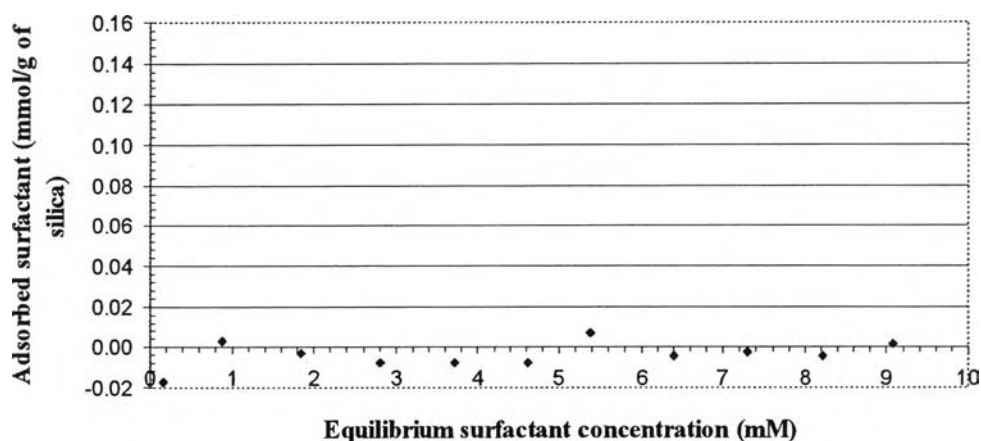


**Figure 4.7** Surface tension versus concentration curve comparison for the investigated surfactants.

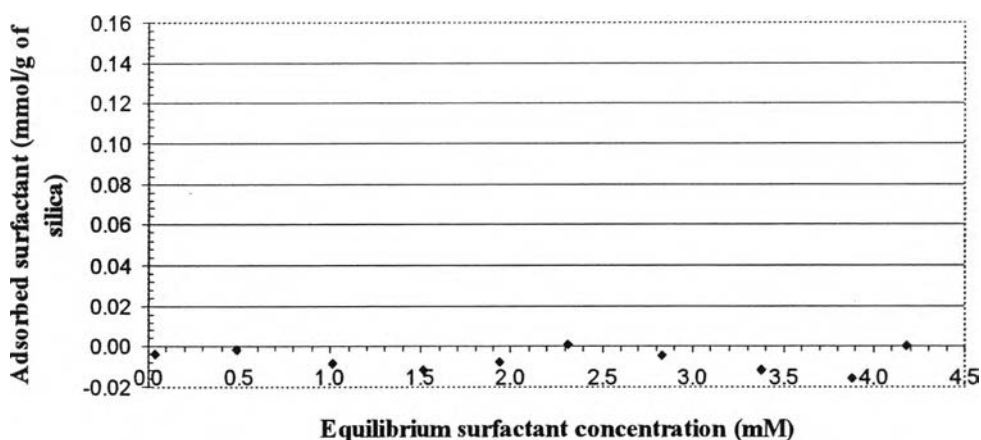
## 4.2 Adsorption of surfactants onto silica

### 4.2.1 Adsorption isotherms of surfactants with HLB in a range of 1-7

The adsorption isotherm of Pluronics L31 (PEO<sub>1</sub>PPO<sub>17</sub>PEO<sub>1</sub>, triblock copolymers, HLB 6.8) and Pluronics 17R2 (PPO<sub>15</sub>PEO<sub>10</sub>PPO<sub>15</sub>, reversed triblock copolymers, HLB 6) onto silica at 29°C are shown in Figures 4.8 and 4.9, respectively.



**Figure 4.8** Adsorption isotherm of Pluronics L31 onto silica at 29°C.



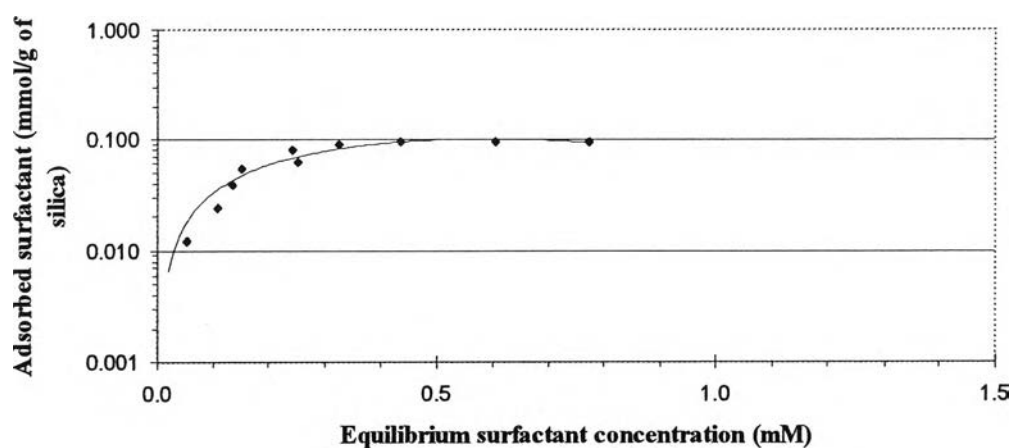
**Figure 4.9** Adsorption isotherm of Pluronics 17R2 onto silica at 29°C.

Pluronics L31 and Pluronics 17R2 do not significantly adsorb onto the silica surface under these conditions, which is consistent with their configurations. Pluronics L31; triblock copolymers; has a low number of EO units and thus there is

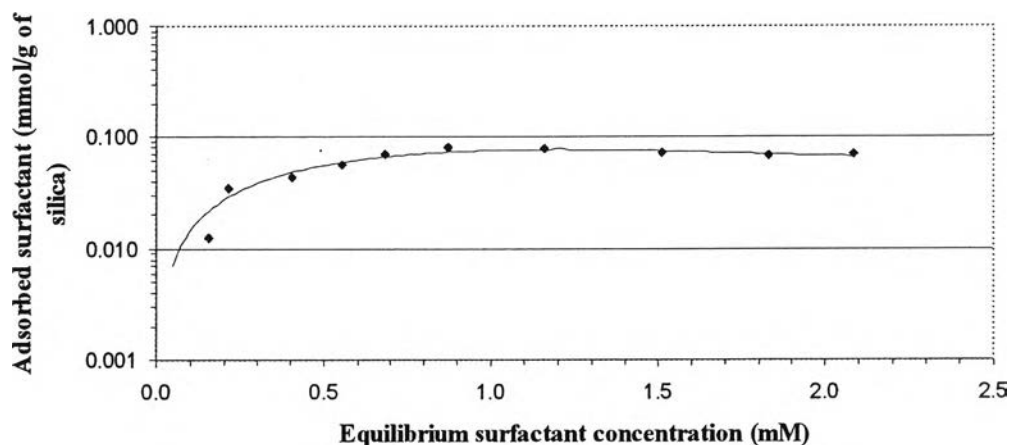
insufficient interaction between the polar EO portion of the surfactant molecule and the polar silica surface. Pluronic 17R2; a reversed triblock copolymers; does not adsorb well due to the low number of EO units and the location of the PEO groups in the middle of the structure, which inhibits interactions with the surface.

#### 4.2.2 Adsorption isotherms of surfactants with HLB in a range of 7-12

The adsorption isotherms of Pluronic P123 ( $\text{PEO}_{19}\text{PPO}_{69}\text{PEO}_{19}$ , triblock copolymers, HLB 8) and Pluronic 25R4 ( $\text{PEO}_{19}\text{PPO}_{33}\text{PEO}_{19}$ , reversed triblock copolymers, HLB 8) at  $29^\circ\text{C}$  are shown in Figures 4.10 and 4.11, respectively. For Pluronic P123, the maximum surfactant adsorption occurs at the equilibrium concentration of 0.42 mM and the maximum adsorbed surfactant is 0.08 mmol of surfactant per gram of silica. For Pluronic 25R4, the maximum surfactant adsorption occurs at an equilibrium concentration of 0.85 mM and the maximum adsorbed surfactant is around 0.064 mmol of surfactant per gram of silica.



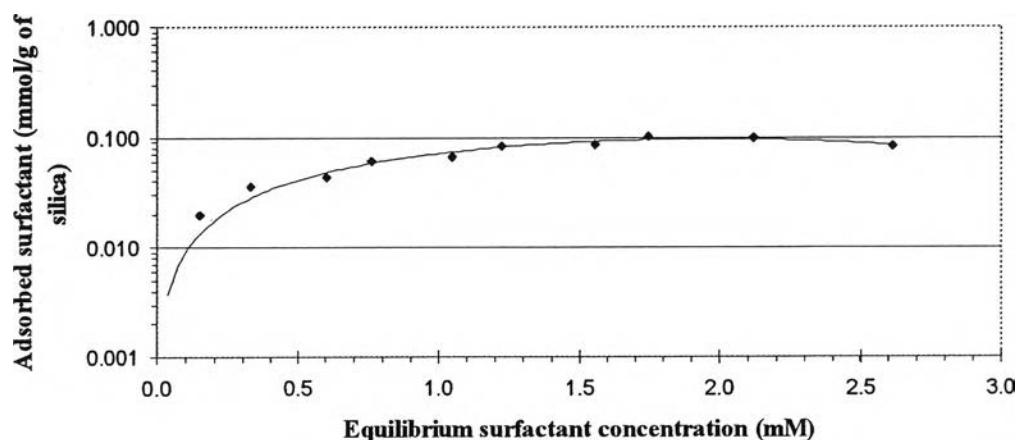
**Figure 4.10** Adsorption isotherm of Pluronic P123 onto silica at  $29^\circ\text{C}$ .



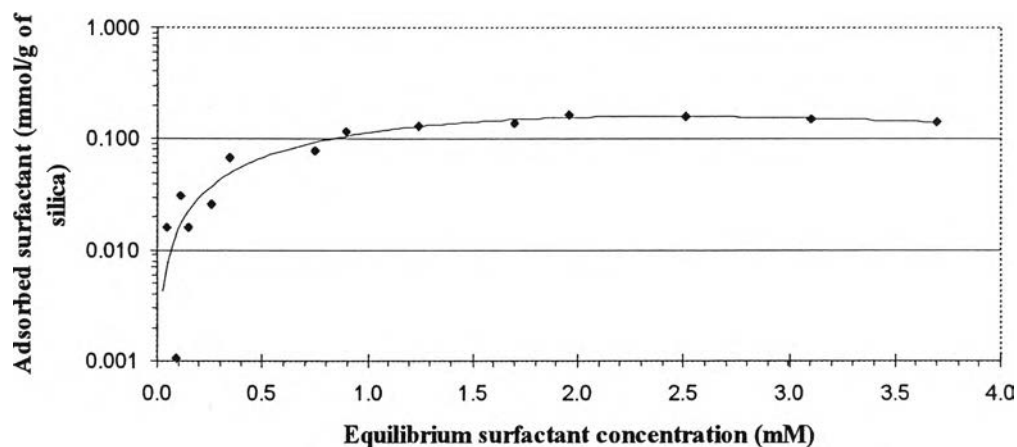
**Figure 4.11** Adsorption isotherm of Pluronic 25R4 onto silica at 29°C.

#### 4.2.3 Adsorption isotherms of surfactants with HLB in a range of 12-18

The adsorption isotherms of Pluronic L64 ( $\text{PEO}_{13}\text{PPO}_{30}\text{PEO}_{13}$ , triblock copolymers, HLB 15) and Pluronic 10R5 ( $\text{PEO}_8\text{PPO}_{23}\text{PEO}_8$ , reversed triblock copolymers, HLB 15) at 29°C are shown in Figures 4.12 and 4.13, respectively. For Pluronic L64, the maximum surfactant adsorption occurs at the equilibrium concentration of 1.75 mM and the maximum adsorbed surfactant is 0.08 mmol of surfactant per gram of silica. For Pluronic 10R5, the maximum surfactant adsorption occurs at the equilibrium concentration of 2 mM and the maximum adsorbed surfactant is 0.12 mmol of surfactant per gram of silica.



**Figure 4.12** Adsorption isotherm of Pluronic L64 onto silica at 29°C.



**Figure 4.13** Adsorption isotherm of Pluronic 10R5 onto silica at 29°C.

The adsorption of block copolymers onto hydrophilic silica occurs for those tested copolymers which fall into the HLB range of 7-18. The results show that block copolymers with HLB values lower than 7 do not appreciably adsorb due to the small number of EO groups capable of interacting with the silica surface. D. Tsurumi *et al.* (2006) showed that block copolymers with HLB values higher than 18 do not adsorb well onto silica due to their high affinity for the aqueous phase. Thus, the optimum range of HLB value which allows block copolymers to adsorb onto silica is 7-18.

The adsorption isotherms of block copolymers illustrate Langmuir characteristic, increasing without apparent breaks until it reaches a plateau. The Langmuir equation is expressed as:

$$Q = \frac{Q_{\max} \cdot Kc}{1 + K \cdot c} \quad (1)$$

where  $K$  = Langmuir equilibrium constant ( $\text{mM}^{-1}$ ),  $c$  = aqueous concentration (mM),  $Q$  = amount adsorbed (mmol/g), and  $Q_{\max}$  = maximum amount adsorbed (mmol/g). The Langmuir parameters for the adsorption of block copolymer surfactants onto silica surface, which are derived by linear regression of Langmuir equation from the experimental values, are shown in Table 4.1.

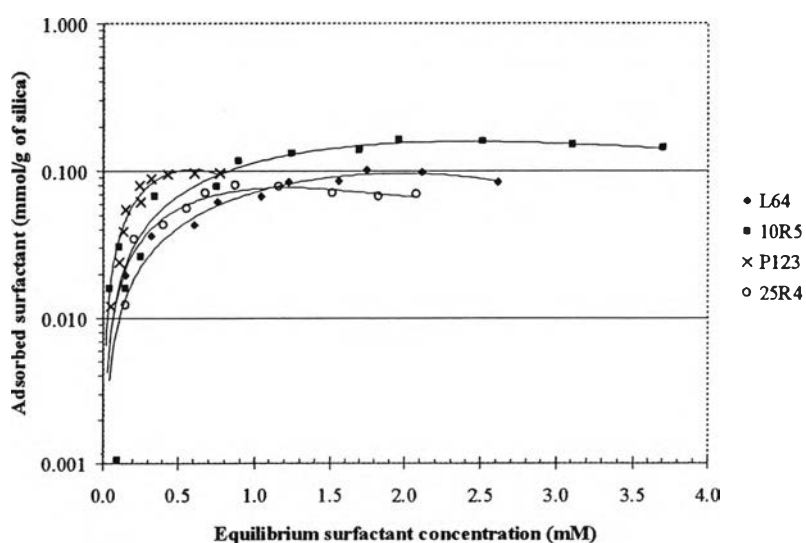


**Table 4.1** The Langmuir parameters for the adsorption of block copolymer surfactants onto silica surface

Copolymer surfactants	Langmuir parameters	
	Q <sub>max</sub> (mmol/g of silica)	K (mM <sup>-1</sup> )
L64	0.0964	1.3959
10R5	0.1579	1.6363
P123	0.1023	3.5344
25R4	0.0772	2.8701

The Langmuir parameters illustrate the adsorption characteristic of copolymer surfactants onto hydrophilic silica. The Langmuir equilibrium constant (K) shows the affinity of surfactants to adsorb onto the solid surface. The higher K value expresses stronger interactions with the surface. The data shows that Pluronic P123 has the strongest interaction, followed by Pluronic 25R4, Pluronic 10R5, and Pluronic L64, respectively. Moreover, the maximum amount of adsorbed surfactants, derived from the Langmuir equation, correlates well with the experimental values.

The adsorption isotherms of the various copolymer surfactants onto silica surface may be compared in Figure 4.14



**Figure 4.14** Comparison of the adsorption isotherms.

The four factors considered in this study for the adsorption of block copolymers onto silica are HLB value, configuration, EO/PO ratio, and molecular weight. Lower HLB values tend to have higher in adsorption affinity than those with the lower HLB values. For a given HLB value but different in configuration, the affinity and the amount of adsorbed surfactant onto a silica particle are influenced by the EO/PO ratio of surfactants more than their molecular weight where the affinity shows the same trend with its Langmuir parameter. The adsorption by surfactants containing a higher EO/PO ratio shows that the presence of PEO groups facilitates adsorption onto the silica surface, as is expected. Configuration also seems to be a factor, since the reversed triblock copolymers are more difficult to adsorb onto the silica surface because the PEO groups are in the middle of the structure. They require higher equilibrium surfactant concentration in order to reach maximum adsorption, which is correlated to the higher CMC required. Changing HLB values does not have an impact on the maximum adsorption, though those with lower CMC values adsorb more readily at lower concentrations, as is expected.

The maximum amount of adsorbed surfactant is thus affected by the copolymer configuration, EO/PO ratio, and molecular weight. The lowest molecular weight and the highest EO/PO ratio (Pluronic 10R5) have the largest adsorbed amounts. This is most likely because the small molecule can easily adsorb onto the surface and the high EO/PO ratio means it interacts well with the polar silica surface. The normal triblock copolymers with different HLB values (Pluronic L64 [HLB 15] and (Pluronic P123 [HLB 8]) all have similar maximum amounts of adsorbed surfactant, even though they have different EO/PO ratios and molecular weights. Pluronic L64 has the lower molecular weight and the higher EO/PO ratio, promoting adsorption. Pluronic P123, which has a lower EO/PO ratio and also a higher molecular weight, also has a low HLB value and CMC. It adsorbs at lower concentrations and reaches the same plateau amount as Pluronic L64. Pluronic 25R4, which has the lowest EO/PO ratio and reversed structure, does not adsorb readily due to the small number of EO units in the molecule.

### 4.3 Adsolubilization of organics

#### 4.3.1 Adsolubilization of organics

The plateau amounts of adsorbed copolymer surfactants onto silica are shown in Table 4.2. Pluronic 10R5 has the highest adsorption amounts, followed by Pluronic L64 and Pluronic P123, and Pluronic 25R4, respectively.

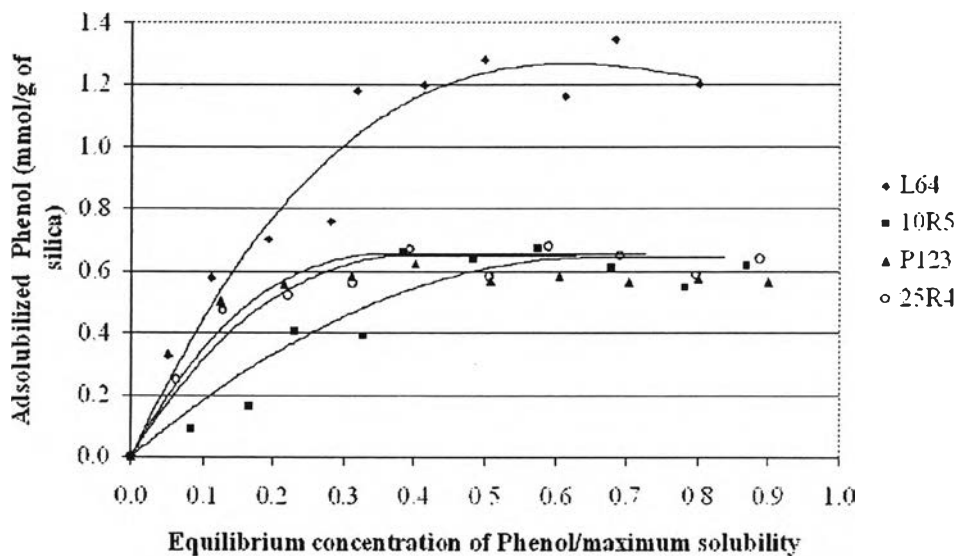
**Table 4.2** The maximum adsorbed copolymer surfactants onto silica

Copolymer surfactants	Maximum adsorbed surfactants (mmol/g of silica)
Pluronic L64	0.08
Pluronic 10R5	0.12
Pluronic P123	0.08
Pluronic 25R4	0.064

##### 4.3.1.1 Adsolubilization of phenol

Phenol was found not to adsorb in any significant degree directly onto the bare silica surface (G.M. Forland and A.M. Blokhus, 2007). Therefore, the amount of adsolubilized phenol versus its reduced bulk concentration (bulk concentration / water solubility) is shown in Figure 4.15. The data illustrates that the maximum phenol adsolubilized in the adsorbed layers of Pluronic L64, Pluronic 10R5, Pluronic P123, and Pluronic 25R4 are 1.13, 0.65, 0.74, and 0.70 mmol of phenol/g of silica, respectively. The maximum values of the ratio of adsolubilized phenol to adsorbed surfactant are compared in Table 4.3 for the various copolymers. The maximum ratio appears to be 5 – 14 mmol of adsolubilized phenol/mmol of adsorbed surfactant, which is significantly high compared to phenol adsolubilization in other conventional surfactants [0.18 mmol of phenol adsolubilized/mmol of SDS, in surfactant-modified alumina (Adak *et al.*, (2005))]. The reason for this was discussed by Nagarajan *et al.* (1985) that aromatic compounds found in the non-polar region of copolymer tails more compatible than the non-polar portion of other conventional surfactants. In addition, Pluronic L64 seems to have the highest amount of phenol

adsolubilized in its adsorbed layer compared to other types of block copolymers in this study.



**Figure 4.15** The adsolubilization of phenol in the examined surfactants.

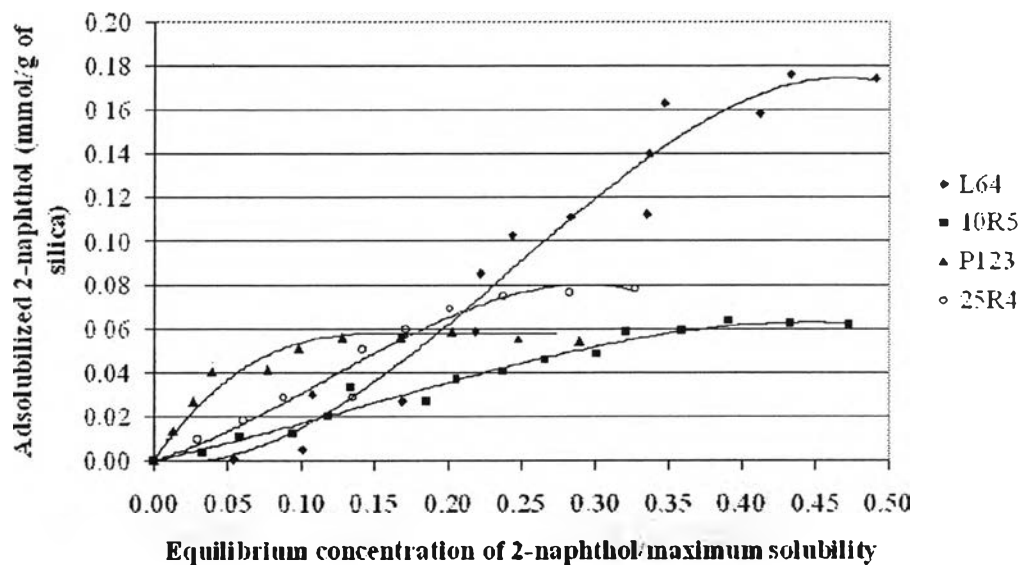
**Table 4.3** The maximum adsolubilized phenol with respect to surfactant concentration

Copolymer surfactants	Maximum adsolubilization ratio (mmol of adsolubilized phenol/ mmol of adsorbed surfactant)
Pluronics L64	14.14
Pluronics 10R5	5.41
Pluronics P123	9.27
Pluronics 25R4	10.92

#### 4.3.1.2 Adsolubilization of 2-naphthol

K. Esumi *et al.*, (2007) found that 2-naphthol was not adsorbed in any significant degree directly onto the bare silica surface. Therefore, the adsolubilized 2-naphthol versus its reduced bulk concentration is shown in Figure 4.16. The data illustrate that the maximum 2-naphthol adsolubilized in the adsorbed

layers of Pluronic L64, Pluronic 10R5, Pluronic P123, and Pluronic 25R4 are 0.17, 0.06, 0.06, and 0.08 mmol of 2-naphthol/g of silica, respectively. The maximum values of the ratio of adsolubilized 2-naphthol to adsorbed surfactant are compared in Table 4.4 for the various copolymers. The maximum ratio appears to be 0.5 – 2 mmol of adsolubilized 2-naphthol/mmol of adsorbed surfactant, which is significantly high compared to 2-naphthol adsolubilization in other conventional surfactants [0.06 mmol of 2-naphthol adsolubilized/mmol of 2RenQ, in surfactant-modified laponite (Esumi *et al.*, (1999)), 0.1 mmol of 2-naphthol adsolubilized/mmol of SDS, in surfactant-modified TiO<sub>2</sub> (Esumi *et al.*, (1998))]. The reason for this was discussed by Nagarajan *et al.* (1985) as described above. In addition, Pluronic L64 again seems to have the highest amount of 2-naphthol adsolubilized in its adsorbed layer compared to other types of block copolymers in this study.



**Figure 4.16** The adsolubilization of 2-naphthol in the examined surfactants.

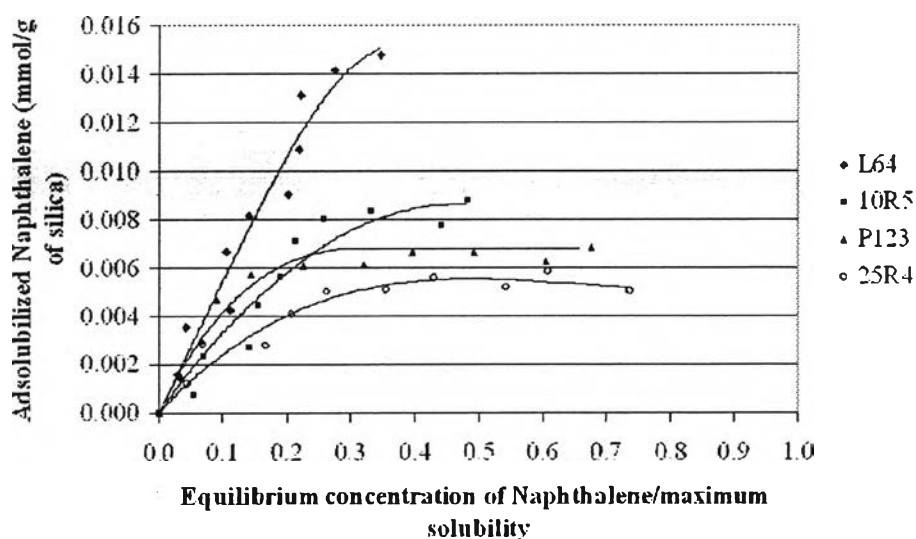
**Table 4.4** The maximum adsolubilized 2-naphthol with respect to surfactant concentration

Copolymer surfactants	Maximum adsolubilization ratio (mmol of adsolubilized 2-naphthol/ mmol of adsorbed surfactant)
Pluronic L64	2.16

Pluronic 10R5	0.52
Pluronic P123	0.73
Pluronic 25R4	1.25

#### 4.3.1.3 Adsolubilization of naphthalene

The adsolubilization of naphthalene versus its reduced bulk concentration is shown in Figure 4.17. The data shows that the maximum adsolubilization of naphthalene in the adsorbed layers of Pluronic L64, Pluronic 10R5, Pluronic P123, and Pluronic 25R4 are 0.015, 0.009, 0.007, and 0.005 mmol of naphthalene/g of silica, respectively. The maximum ratios of adsolubilized naphthalene to adsorbed surfactant are compared in Table 4.5. The ratios range from 0.08 – 0.18 mmol of adsolubilized naphthalene/mmol of adsorbed surfactant, which is approximately the same to ratios observed for naphthalene in conventional surfactants [0.03 mmol of naphthalene adsolubilized/mmol of 1RQ, in surfactant-modified TiO<sub>2</sub> (Esumi *et al.*, (1997)), 0.14 mmol of naphthalene adsolubilized/mmol of 2RenQ, in surfactant-modified TiO<sub>2</sub> (Esumi *et al.*, (1997))]. In addition, Pluronic L64 again seems to have the highest amount of 2-naphthol adsolubilized in its adsorbed layer compared to other types of block copolymers in this study.



**Figure 4.17** The adsolubilization of naphthalene in the examined surfactants.

**Table 4.5** The maximum adsolubilized 2-naphthol with respect to surfactant concentration

Copolymer surfactants	Maximum adsolubilization ratio (mmol of adsolubilized naphthalene/ mmol of adsorbed surfactant)
Pluronics L64	0.188
Pluronics 10R5	0.075
Pluronics P123	0.085
Pluronics 25R4	0.081

Block copolymer surfactants appear to have higher adsolubilization capacities for aromatic compounds, especially with small organic molecules or polar substances, than the adsorbed layers of other conventional surfactants. This is because small molecules can easily be adsolubilized and polar molecules strongly interact with the polar portions of the adsorbed block copolymers. In addition, the better compatibility of aromatic compounds in the non-polar region of copolymer tails than in the non-polar portion of other conventional surfactants is the main reason for the higher amounts of organics adsolubilization (Nagarajan *et al.*, 1985).

The affinity of phenol, 2-naphthol, and naphthalene to be adsolubilized onto the adsorbed layers of copolymer surfactants is influenced by the number of PPO groups and the molecular weights of the copolymers themselves. For a given HLB value, copolymers which have larger number of PPO groups and higher molecular weight appear to adsolubilize organics appreciably more than those with a lower number of PPO groups and lower molecular weight. The maximum amounts of adsolubilized organics are most likely to be the same for the adsorbed layers of Pluronics 10R5, P123, and 25R4. On the other hand, Pluronics L64 is surprisingly different. It appears to have many times higher adsolubilization capacity for organics than the other tested copolymer surfactants. Some possible reasons are shown in table 4.6. For a given HLB value (HLB 15), although Pluronics L64 has the smaller

level of adsorption compared to Pluronics 10R5, it shows much larger amounts of adsolubilized organics. It could be because Pluronics L64 has PO segments that are two times those of Pluronics 10R5. Comparing Pluronics L64 and Pluronics 25R4, they have almost the same unit numbers of EO and PO portions in the molecular structures but show different amounts of adsorption, Pluronics 25R4 has lower adsorption than Pluronics L64, which could contribute to the same outcome. The difference of organic adsolubilized of Pluronics L64 and Pluronics P123 is almost three times higher for Pluronics L64. We are unsure of the reason for this though it could be the consequence of the difference in EO/PO ratio. Pluronics L64 has higher EO/PO ratio than that of Pluronics P123, the higher ratio means the stronger surfactants bound to the silica surface. Therefore, while organic solutes are being adsolubilized in the adsorbed layer, the interaction force between non-polar portion of the solute molecules and the hydrophobic part of surfactants are increased. This force might be higher than the attractive force between EO portion of surfactants and the silica surface. This may causes the displacement of the adsorbed Pluronics P123 from silica surface which result in the less number of organic adsolubilized in the adsorbed layer of Pluronics P123 than that in the adsorbed layer of Pluronics L64.

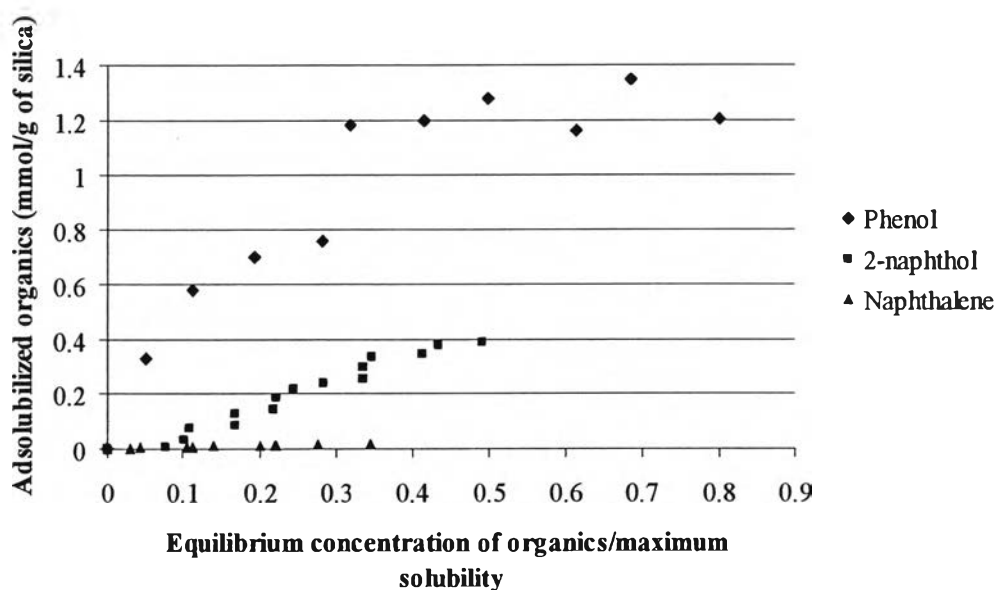
**Table 4.6** Copolymers properties

<b>Copolymer surfactants</b>	<b>HLB values</b>	<b>EO/PO ratio</b>	<b>Structures</b>	<b>Maximum Adsorbed surfactants (mmol/g of silica)</b>
Pluronics L64	15	0.6629	EO13-PO30-EO13	0.08
Pluronics 10R5	15	0.9898	PO8-EO23-PO8	0.12
Pluronics P123	8	0.4286	EO19-PO69-EO19	0.08
Pluronics 25R4	8	0.25	PO19-EO33-PO19	0.064

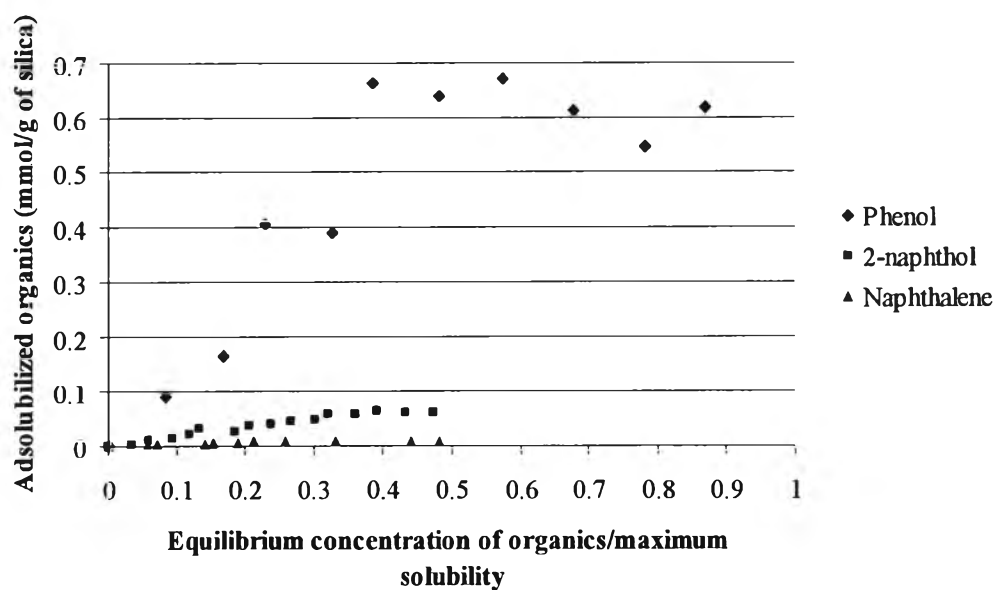


#### 4.3.2 The effects of numbers of rings and polarities to the adsolubilization behaviors

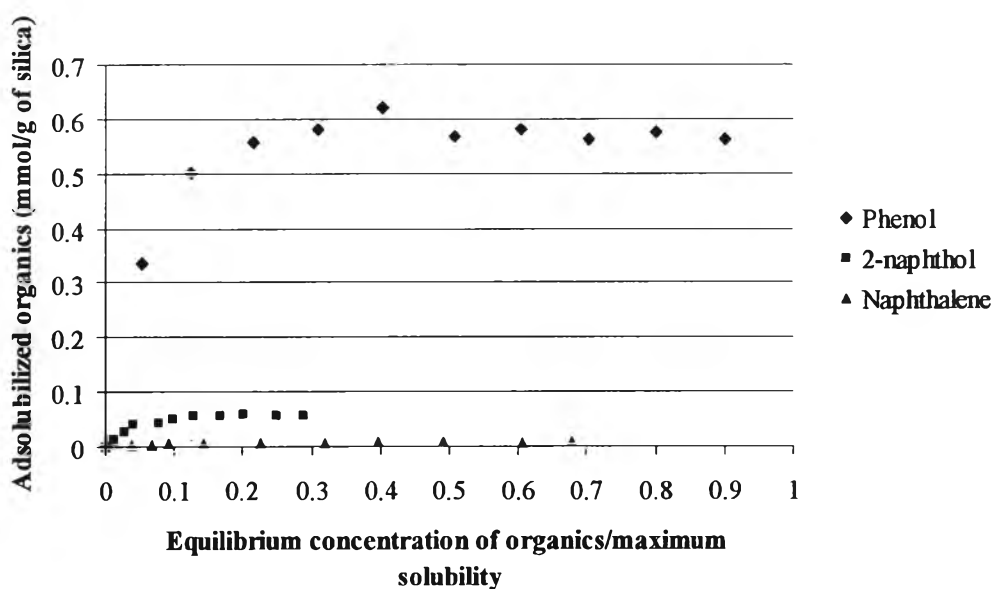
The adsolubilization of phenol, 2-naphthol, and naphthalene in the adsorbed layers of Pluronics L64, Pluronics 10R5, Pluronics P123, and Pluronics 25R4; are shown in Figures 4.18, 4.19, 4.20, and 4.21, respectively.



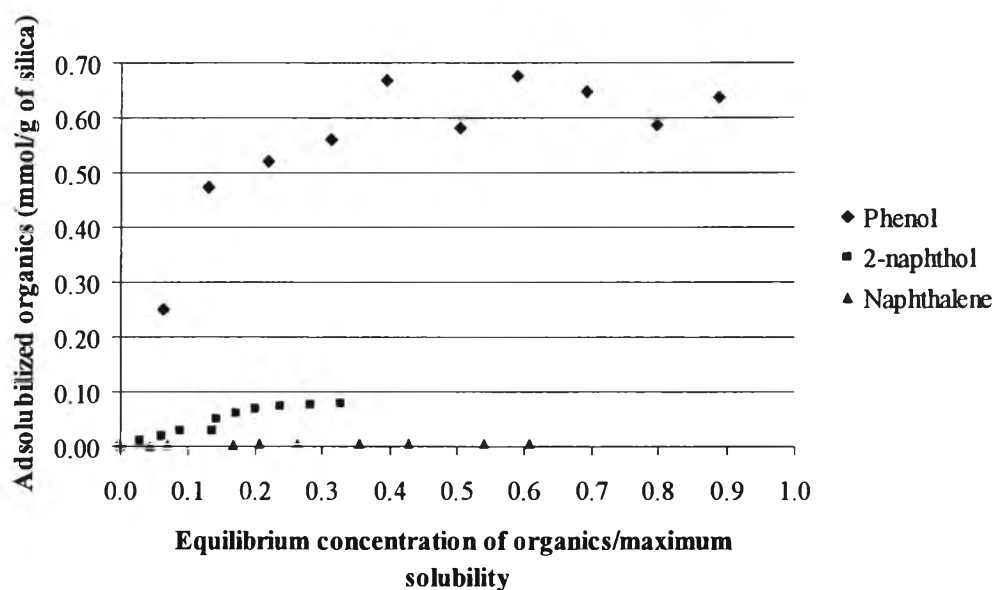
**Figure 4.18** The adsolubilization of phenol, 2-naphthol, and naphthalene onto the adsorbed layer of Pluronics L64.



**Figure 4.19** The adsolubilization of phenol, 2-naphthol, and naphthalene onto the adsorbed layer of Pluronic 10R5.



**Figure 4.20** The adsolubilization of phenol, 2-naphthol, and naphthalene onto the adsorbed layer of Pluronic P123.



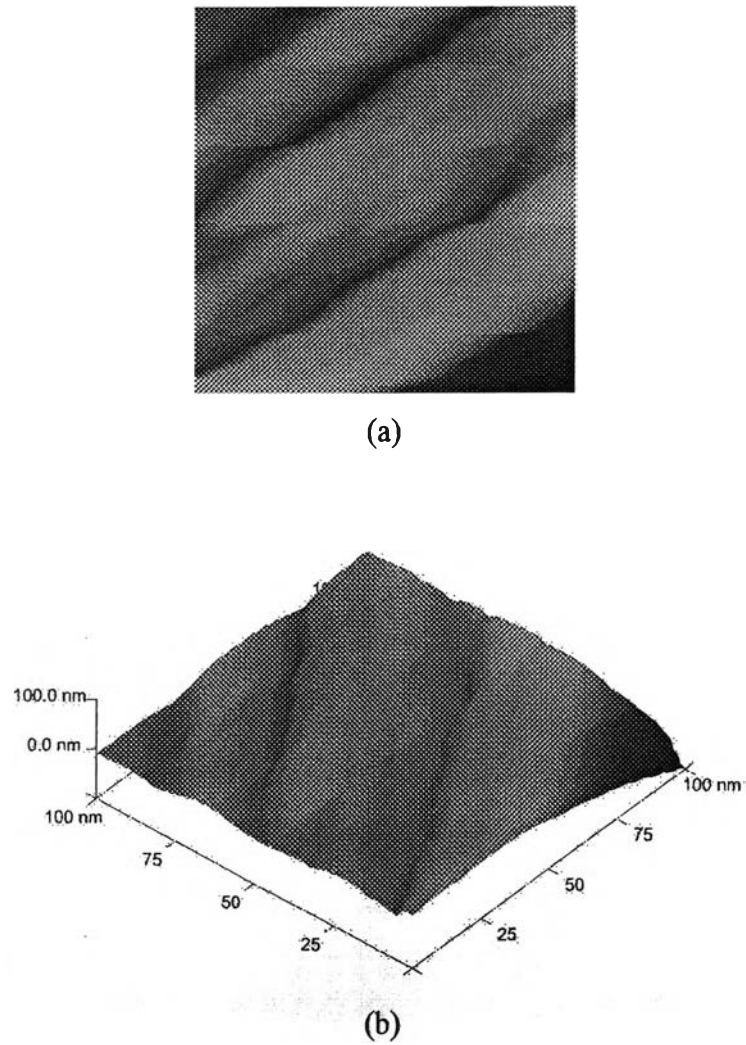
**Figure 4.21** The adsolubilization of phenol, 2-naphthol, and naphthalene onto the adsorbed layer of Pluronic 25R4.

The molecular size of the solute, primarily due to the numbers of aromatic rings, has an enormous effect on the amounts of adsolubilization, as is expected. The smaller molecules have higher amounts of adsolubilization than do the larger ones because they “fit” more easily within the adsorbed layers and take up less of the adsolubilization capacity. Therefore, phenol, the smallest solute tested and having a single benzene ring, adsolubilized to a much higher degree than did 2-naphthol and naphthalene which have polyaromatic ring structures.

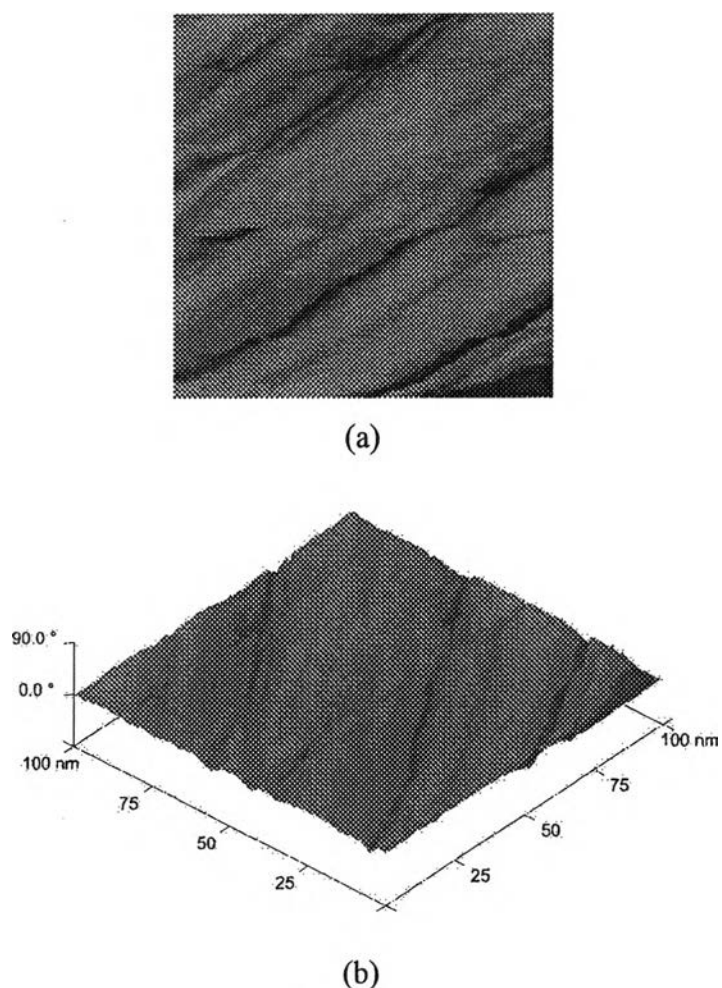
The effect of solute polarity as seen in 2-naphthol and naphthalene, which have the same numbers of aromatic rings, has a significant impact on their adsolubilization. Naphthalene has approximately  $1/10^{\text{th}}$  the adsolubilization of 2-naphthol. This is because polar compounds are capable of adsolubilizing in both the palisade and core regions of the adsorbed aggregates, while the non-polar solutes should partition primarily only into the core regions of the adsorbed aggregates. Consequently, both numbers of aromatic rings and polarities seem to be the factors that contribute to the differences in the organic adsolubilization behaviors as is expected.

#### 4.4 Determination of surface characteristics by using AFM

The topography images and the phase images of unmodified silica are shown in figure 4.22 and 4.23, respectively.



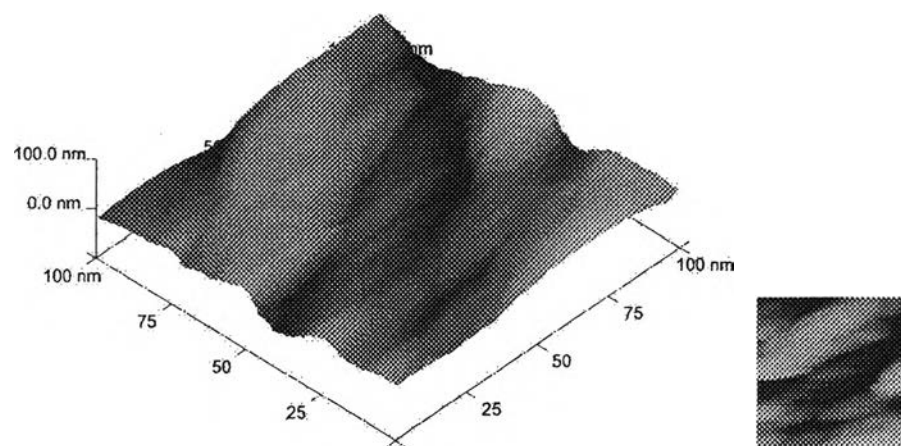
**Figure 4.22** Topography images of unmodified silica: (a) 2-dimensional image (100nm x 100nm), (b) 3-dimensional image (100nm x 100nm x 100nm).



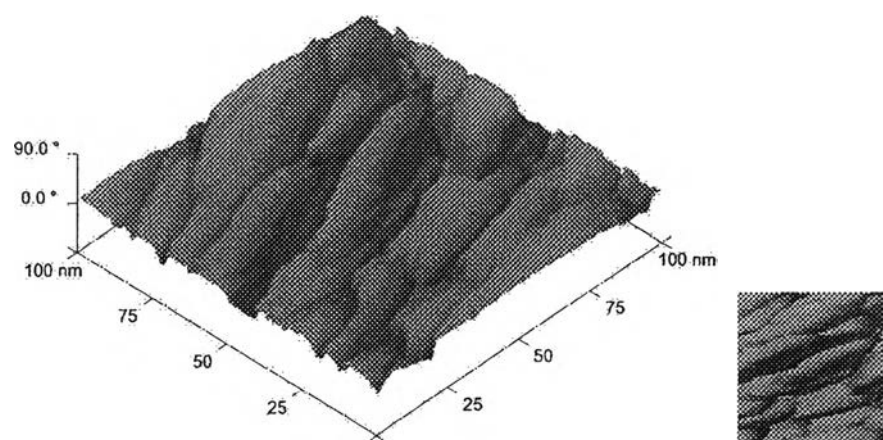
**Figure 4.23** Phase images of unmodified silica: (a) 2-dimensional image (100nm x 100nm, 90°), (b) 3-dimensional image (100nm x 100nm x 90°).

AFM topography shows color mapping for height image data in nano-scale surfaces, and phase image detects variations in compositions and other properties information about the surface structures. The topography images of the unmodified silica in Figure 4.22 shows the differences in height due to the curvature of silica particle. In addition, no significant phase variation of the unmodified silica is observed in Figure 4.23.

The topography images and the phase images of silica modified with Pluronic L64, Pluronic 10R5, Pluronic P123, and Pluronic 25R4 are shown in Figures 4.24, 4.25, 4.26, and 4.27, respectively.

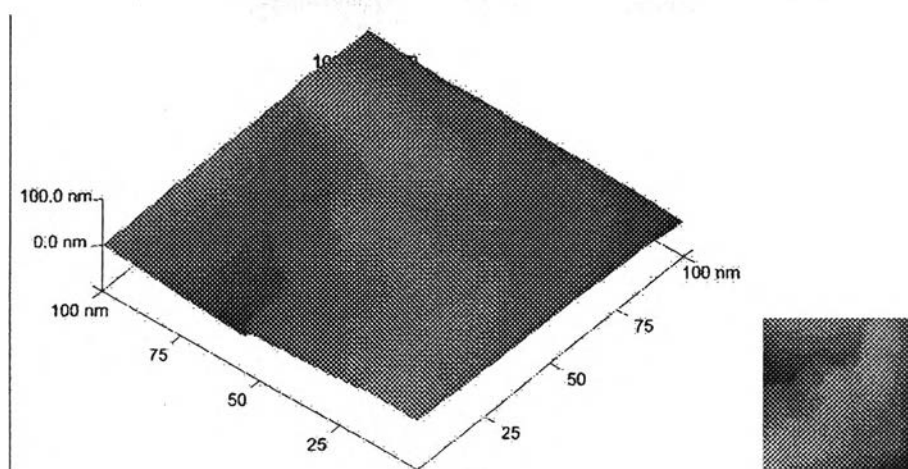


(a)

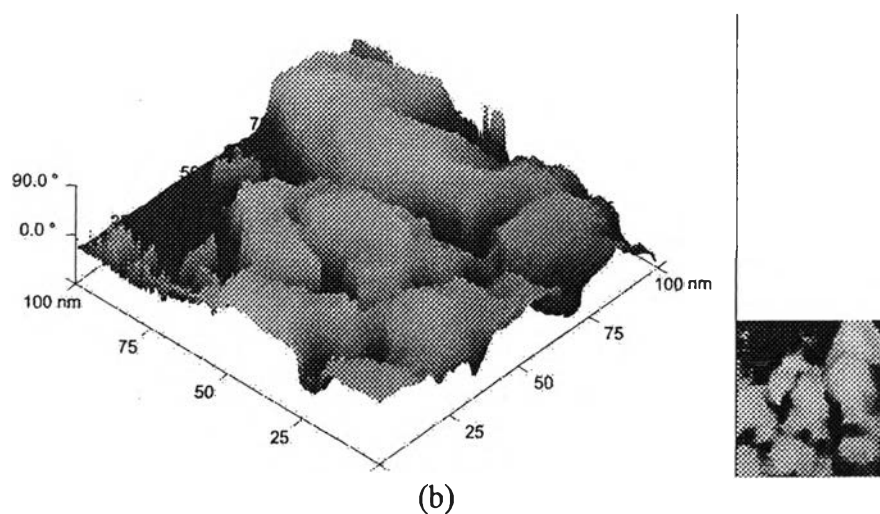


(b)

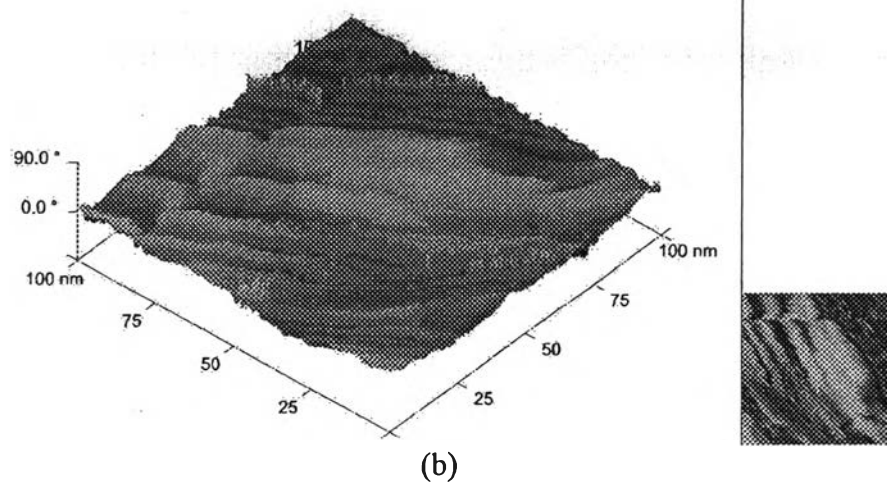
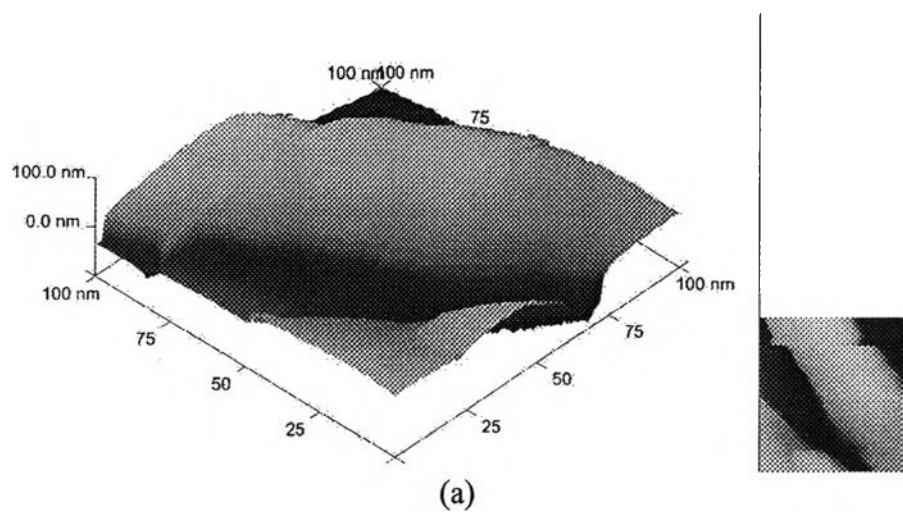
**Figure 4.24** Images of the silica modified with Pluronic L64: (a) Topography images (100nm x 100nm x 100nm), (b) Phase images (100nm x 100nm x 90°).



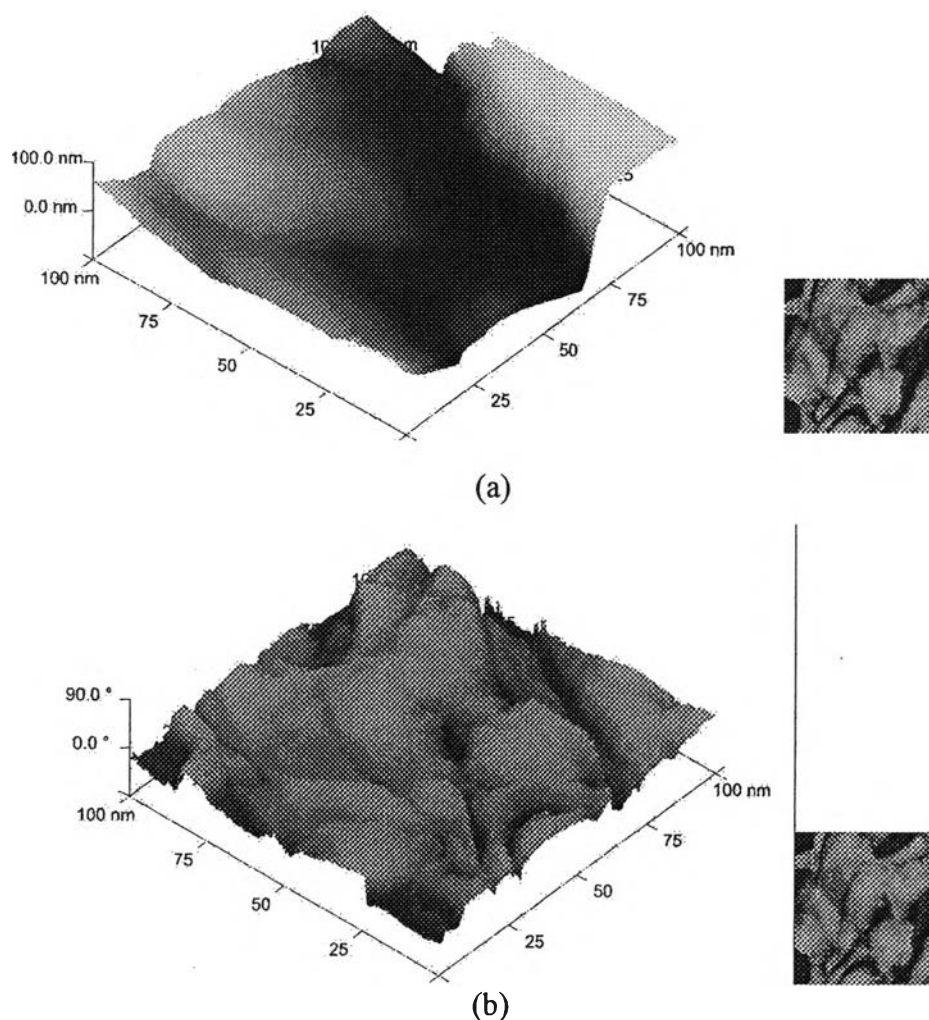
(a)



**Figure 4.25** Images of the silica modified with Pluronic 10R5: (a) Topography images (100nm x 100nm x 100nm), (b) Phase images (100nm x 100nm x 90°).



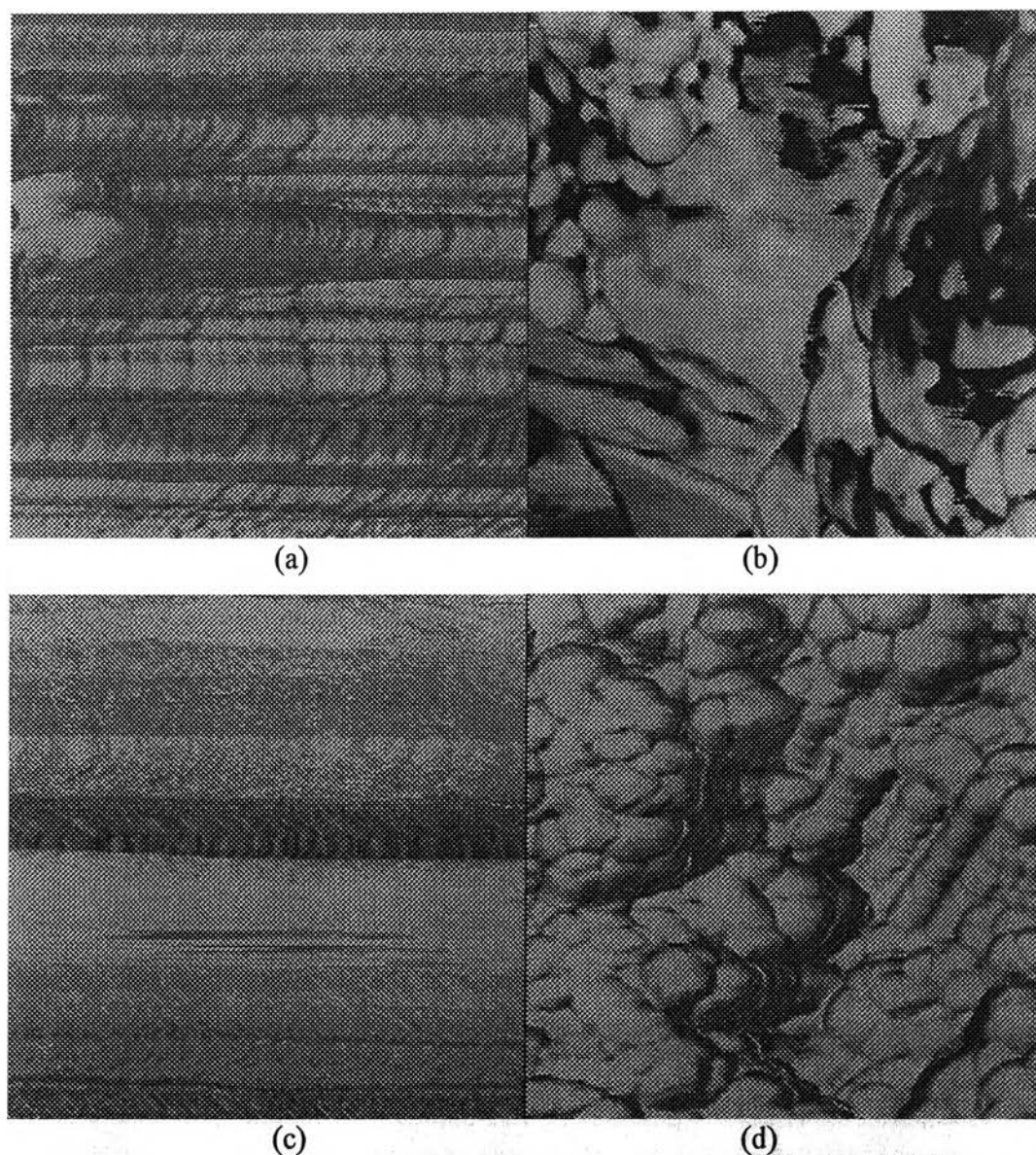
**Figure 4.26** Images of the silica modified with Pluronic P123: (a) Topography images (100nm x 100nm x 100nm), (b) Phase images (100nm x 100nm x 90°).



**Figure 4.27** Images of the silica modified with Pluronic 25R4: (a) Topography images (100nm x 100nm x 100nm), (b) Phase images (100nm x 100nm x 90°).

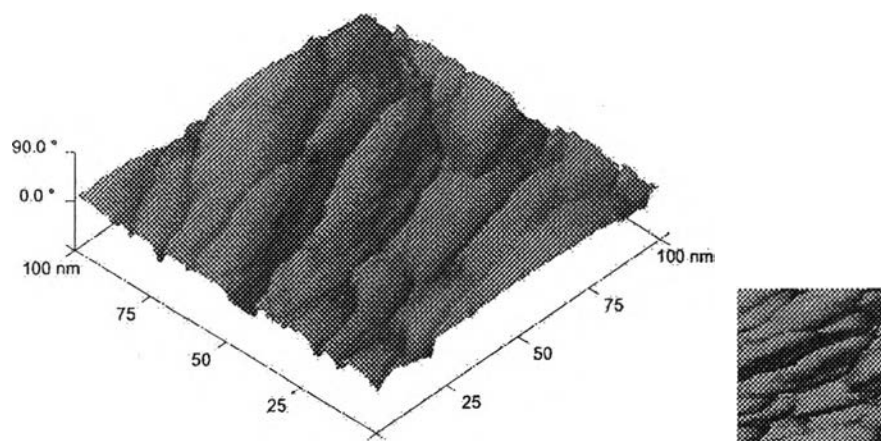
The silica surfaces modified with the various block copolymer surfactants appear to have clusters of copolymers on the silica surfaces. The clusters arrangements of Pluronic L64 and Pluronic P123, which are the triblock copolymers, seem to have better oriented patterns than those of Pluronic 10R5 and Pluronic 25R4, which are the reversed triblock copolymer surfactants, as shown in Figure 4.28. Therefore, the surfactant structures could be the factors that contribute to the cluster orientations of block copolymer surfactants onto hydrophilic silica. Unfortunately, the reason for this is still not yet understood.



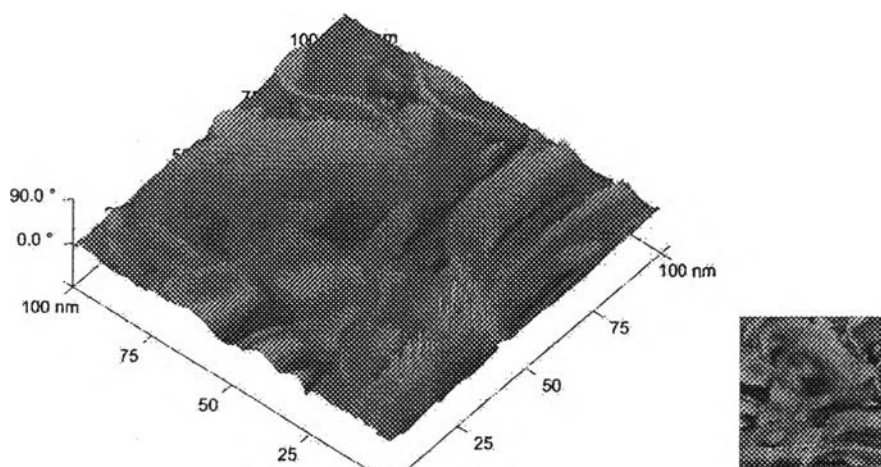


**Figure 4.28** Phase images of the silica modified with Pluronics L64 (a), Pluronics 10R5 (b), Pluronics P123 (c), and Pluronics 25R4 (d), at 300nm x 300nm, 180°.

The phase images of surfactant-modified silica after adsorption of organics are shown in Figures 4.29 and 4.30. Phenol was used as a model organic adsorbed, Pluronics L64 (triblock copolymers) and Pluronics 10R5 (reversed triblock copolymers) were also used as the model of surfactants in surfactant-modified silica.

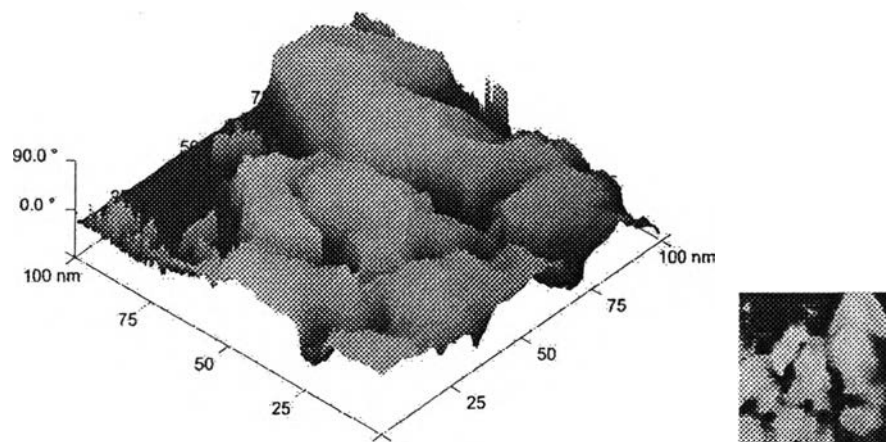


(a)

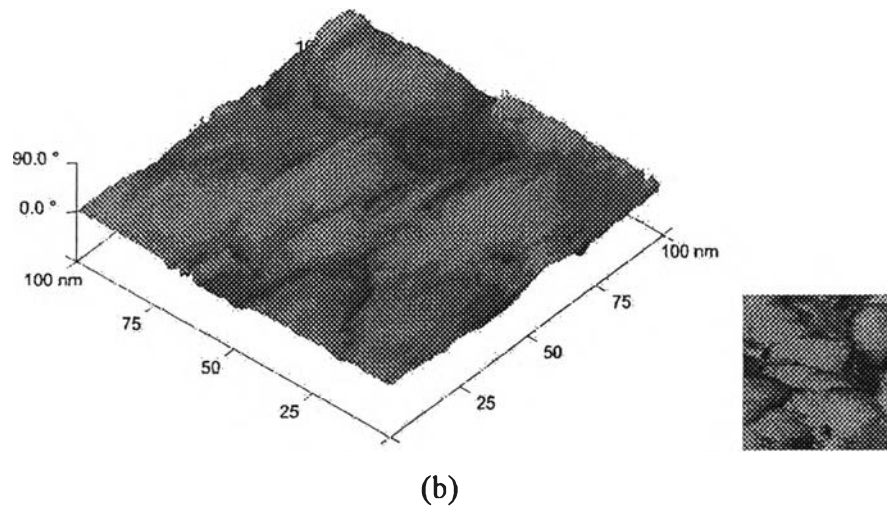


(b)

**Figure 4.29** Phase images of the silica modified with Pluronic L64 (a), and phase images of the silica modified with Pluronic L64 after adsolubilization of phenol (b), at 100nm x 100nm, 90°.



(a)



**Figure 4.30** Phase images of the silica modified with Pluronic 10R5 (a), and phase images of the silica modified with Pluronic 10R5 after adsorption of phenol (b), at 100nm x 100nm, 90°.

After phenol is adsorbed in an adsorbed layer of surfactant modified silica, the copolymer clusters on the silica surfaces tend to change their morphologies to flatter structures than those seen with adsorbed surfactant alone. Mizutani and Tokumoto (1996) discussed that the decrease in phase height resulted from the reduction of repulsive forces between the hydrophilic parts of the adsorbed surfactants (in this case is PEO groups) and the hydrophobic parts of the adsorbed surfactants (in this case is PPO groups). Therefore, phenol which could be adsorbed in the polar region near the PEO groups can reduce the repulsive forces between the polar portions and non-polar portions of the adsorbed copolymer surfactants, which could be the reason of morphological changes of the surfactants-modified silica after organics being adsorbed.