

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Adsorption on Hi-Sil<sup>®</sup>255

In this part of the study, the adsorption of single surfactant and mixed cationic-nonionic surfactants at various ratios on silica Hi-Sil<sup>®</sup>255 were studied.

##### 4.1.1 Single Surfactant

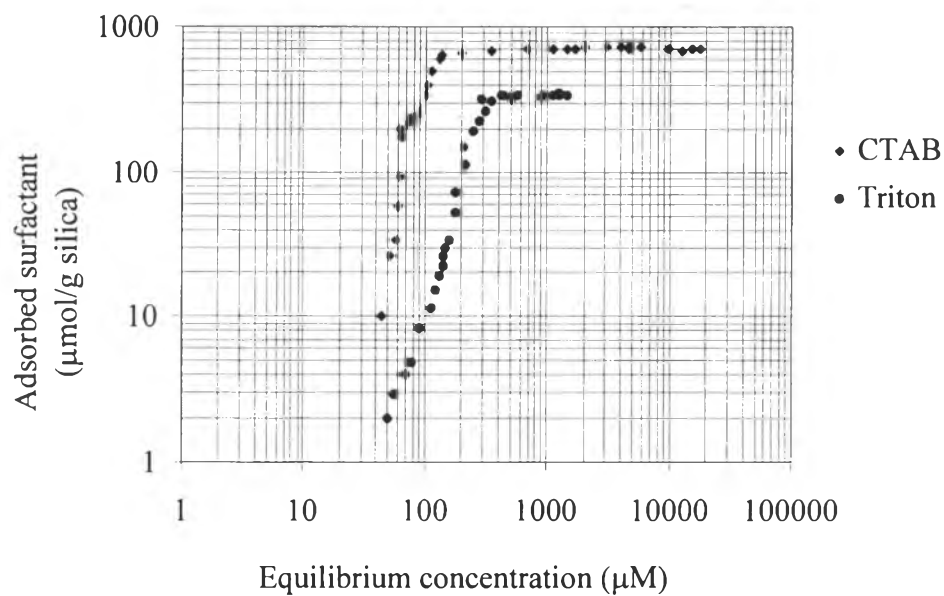
Figure 4.1 shows the surfactant adsorption isotherms of CTAB and Triton on Hi-Sil<sup>®</sup>255 at pH 8 plotted on a log-log scale. All of isotherms illustrate the characteristic regions II, III, IV. The critical micelle concentration (CMC) in CTAB and Triton X-100 are approximately 900 and 300  $\mu\text{M}$ , respectively. For every equilibrium concentration, CTAB adsorption on silica is always higher than the Triton X-100 adsorption. From the plateau region, the maximum CTAB, Triton X-100 adsorption on silica are approximately 700 and 300  $\mu\text{mol/g}$  silica, respectively. This is attributed to the interaction between the surfactant and the silica surface. The dominant interaction between nonionic surfactants and the silica surface is hydrogen bonding between the ether oxygen of the ethylene oxide groups on silica surface, whereas the favorable interaction between the cationic surfactant and silica surface is electrostatically driven (Penfold *et al.*, 1997).

##### 4.1.2 Mixed Surfactant

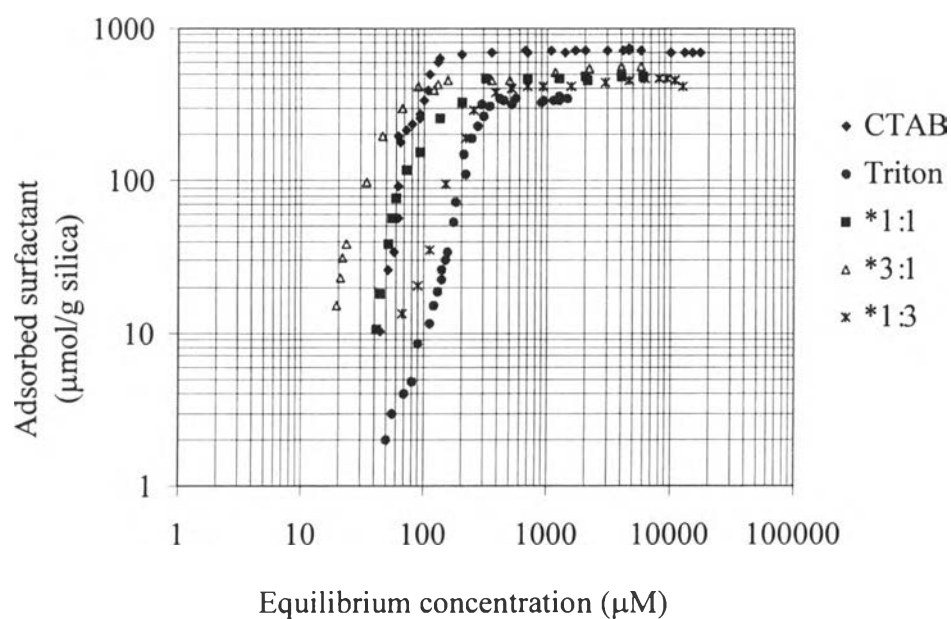
The results from the adsorption of mixed surfactants on Hi-Sil<sup>®</sup>255 can be presented in terms of the total surfactant (combined CTAB and Triton) as well as each surfactant separately.

###### 4.1.2.1 *Total Surfactant Adsorption*

Figure 4.2 shows the total surfactant adsorption isotherms of both single and mixed surfactants at pH 8 plotted on a log-log scale. For clarification, total surfactant adsorption is referred to sum of the amount of CTAB



**Figure 4.1** Adsorption isotherms of CTAB and Triton X-100 on Hi-Sil<sup>®</sup>255 at pH 8.



**Figure 4.2** Adsorption isotherms of CTAB, Triton X-100 and mixed surfactant on Hi-Sil<sup>®</sup>255 at pH 8 (\*denotes CTAB).

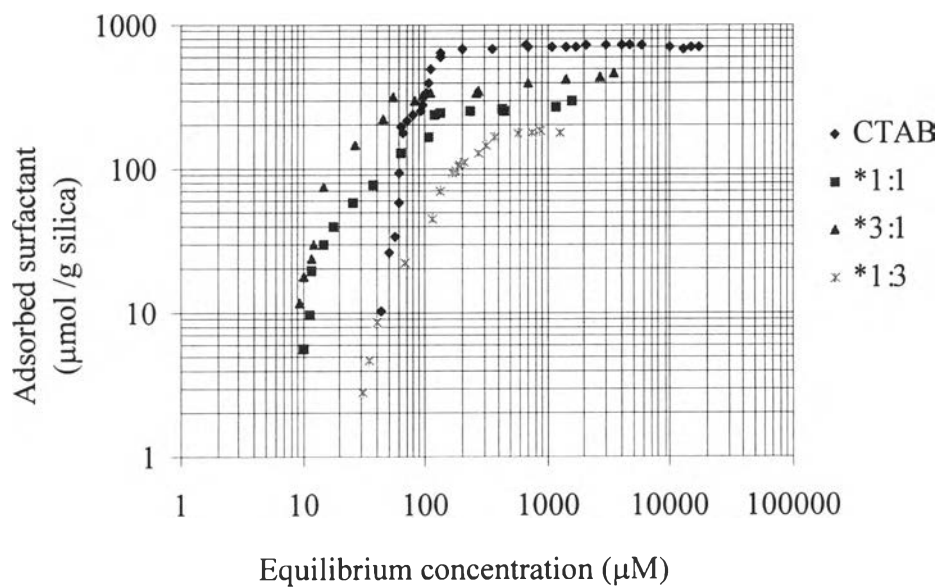
and Triton X-100 adsorption. All isotherms illustrate the characteristic regions II, III, IV. The CMC of the mixed CTAB/Triton systems at the different molar ratios of 3:1, 1:1, 1:3 are quite close, which are approximately 300-400  $\mu\text{M}$ . It is obvious that the addition of Triton to the CTAB in all mixed surfactant systems causes a reduction of the CMC as compared to the pure CTAB system. The maximum surfactant adsorption in CTAB/Triton at ratio 3:1, 1:1, 1:3 are approximately 570, 480 and 400  $\mu\text{mol/g}$  silica, respectively. The amount of each surfactant adsorbed on Hi-Sil<sup>®</sup>255 is quite close to the molar ratio of CTAB/Triton in the mixed systems. For example, in mixed system of CTAB/Triton at ratio 3:1, approximately 75% of the total adsorbed amount of surfactant is CTAB, whereas in mixed system of CTAB/Triton at ratio 1:3, majority of surfactant adsorbed on silica surface is Triton.

#### 4.1.2.2 CTAB Adsorption

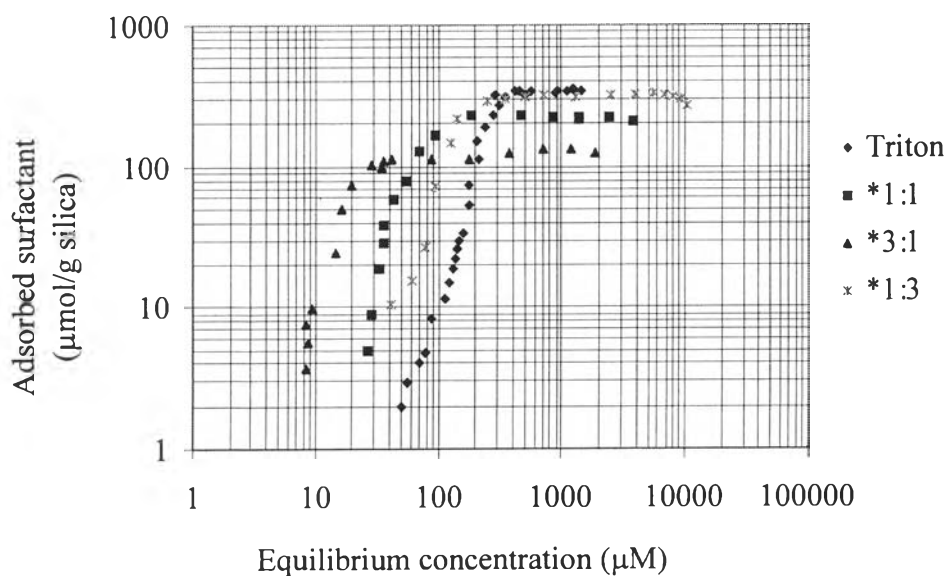
Figure 4.3 shows the adsorption isotherms of CTAB on silica in single (pure) and mixed surfactant systems at pH 8 plotted on a log-log scale. All isotherms illustrate the characteristic regions II, III, IV. In low concentration region, the adsorption of CTAB is slightly enhanced by the addition of Triton in the system in mixed system of CTAB/Triton at ratio 3:1 and 1:1, whereas the adsorption of CTAB in the plateau region decreases with a decrease in CTAB content in the initial mixtures. This is probably due to the competition between Triton and CTAB, which causes the decrease in the adsorption of CTAB with the addition of Triton.

#### 4.1.2.3 Triton X-100 Adsorption

Figure 4.4 shows the adsorption isotherms of Triton on silica in both single- and in mixed-surfactant systems at pH 8 plotted on a log-log scale. All isotherms illustrate the characteristic regions II, III, IV. A decrease in the adsorption of Triton is observed in the plateau region as the molar ratio of Triton is decreased. The adsorption of Triton on the silica surface is enhanced by the presence of cationic surfactant as indicated by the continuous shift of Triton isotherms toward the left with an increase in mole fraction of CTAB. This indicates that an increase in the adsorption sites for Triton as provided by the adsorption of CTAB by electrostatic interaction with the silica surface.



**Figure 4.3** Adsorption isotherms of CTAB on Hi-Sil<sup>®</sup>255 in single system and mixed CTAB/Triton system at ratio 1:1, 3:1, 1:3 (\*denotes CTAB).



**Figure 4.4** Adsorption isotherms of Triton X-100 on Hi-Sil<sup>®</sup>255 in single system and mixed CTAB/Triton system at ratio 1:1, 3:1, 1:3 (\*denotes CTAB).

## 4.2 Adsolubilization Studies

In this part of the study, the adsolubilization of two organic solutes, toluene and acetophenone, into both single- and mixed-surfactants systems of CTAB and Triton X-100 adsorbed on precipitated silica have been performed in two distinct systems, single- and mixed-solute systems. First the equilibrium adsorbed surfactant on silica was carried out at a previously determined equilibrium surfactant concentration in the aqueous solution which was right below the CMC of the system. The organic solute within its aqueous solubility limit was then added to the equilibrium system described above by syringe injection into the crimp-sealed vial. The solubility of toluene and acetophenone at 30°C are 542 ppm and 6842 ppm, respectively (Yaws, 1999).

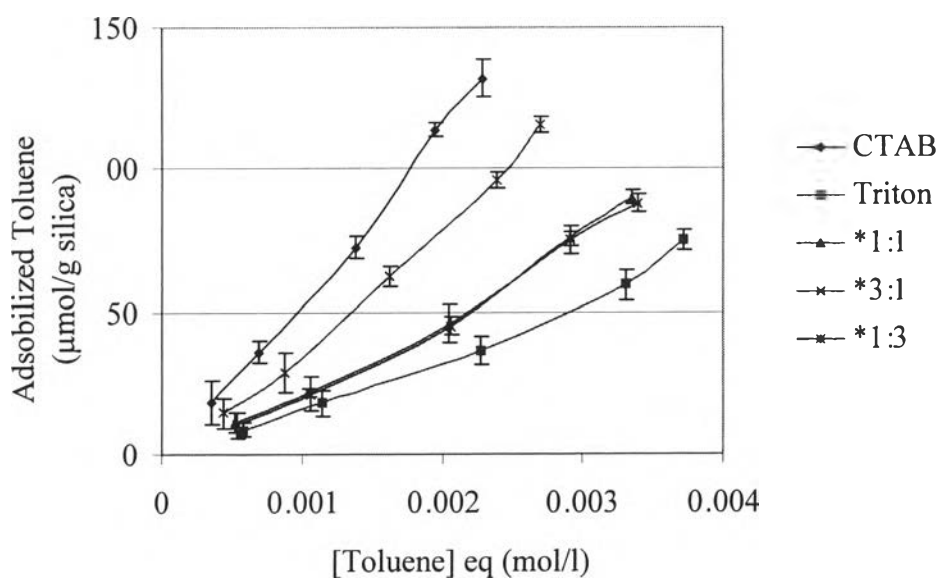
### 4.2.1 Single-Solute Systems

#### 4.2.1.1 *Adsolubilization of Toluene*

A two-step process consisting of surfactant adsorption followed by subsequent adsolubilization of organic solute was used to investigate the adsolubilization characteristics of both single- and mixed-surfactant systems adsorbed on the silica surface for toluene. For the adsolubilization of toluene in the single-solute system, after equilibrium adsorption of surfactant on silica surface, toluene was added to the adsorbed surfactant on silica. After appropriate equilibration time, the amount of toluene remaining in the supernatant was measured by a headspace GC and the adsolubilized amount of toluene was determined using the method of difference.

Figure 4.5 shows the adsolubilization isotherms of toluene that are plots of the adsolubilized amount of toluene versus the equilibrium concentration of toluene in the aqueous phase at pH 8. It can be seen that the adsolubilization of toluene increases with increasing equilibrium concentration of toluene. In single surfactant system, adsolubilization of toluene is highest in the system of CTAB whereas the lowest is observed in the system having Triton alone. In the mixed surfactant system, the presence of Triton X-100 in the system results in lowered toluene adsolubilization. In addition, the adsolubilization of toluene

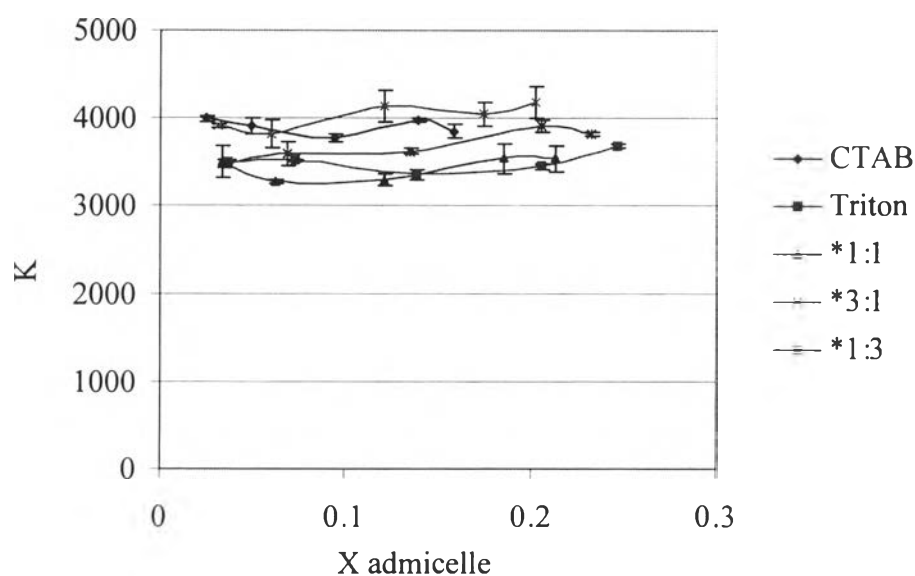
decreases with increasing amount of Triton in the mixed surfactant system. The adsolubilization of toluene observed here seems to be directly related to the amount of surfactant adsorbed on silica surface for both single- and mixed-surfactant systems. As seen in the surfactant adsorption studies, the addition of Triton causes CMC of the mixed surfactant system to be lowered as well as the amount of surfactant adsorbed. Thus, it is not surprising to see lower toluene adsolubilization in the system with the addition of Triton. For example, the amount of adsolubilized toluene in the system having CTAB:Triton of 3:1 is approximately 65% of the system having CTAB alone. This corresponds well with the amount of adsorbed surfactant on silica of the system having CTAB:Triton of 3:1 which is approximately 65% of the amount of adsorbed surfactant in CTAB single system. The lowest adsolubilization of toluene is observed in the system of Triton alone, which also has the lowest surfactant adsorption.



**Figure 4.5** Adsolubilization of toluene in various surfactant systems at pH 8 (\*denotes CTAB).

Figure 4.6 is the plot of the partition coefficient ( $K$ ) versus the mole fraction of toluene in admicelle ( $X_{\text{admicelle}}$ ) at pH 8. The trend observed from the plot shows a very similar behavior in all systems studied. The partition

coefficients remain relatively constant as mole fraction of the toluene in admicelle increases. This indicates that the toluene partitions to both the core and the palisade layer of the admicelle since toluene is a slightly polar organic solute as has been reported (Pradubmook *et al*, 2003).



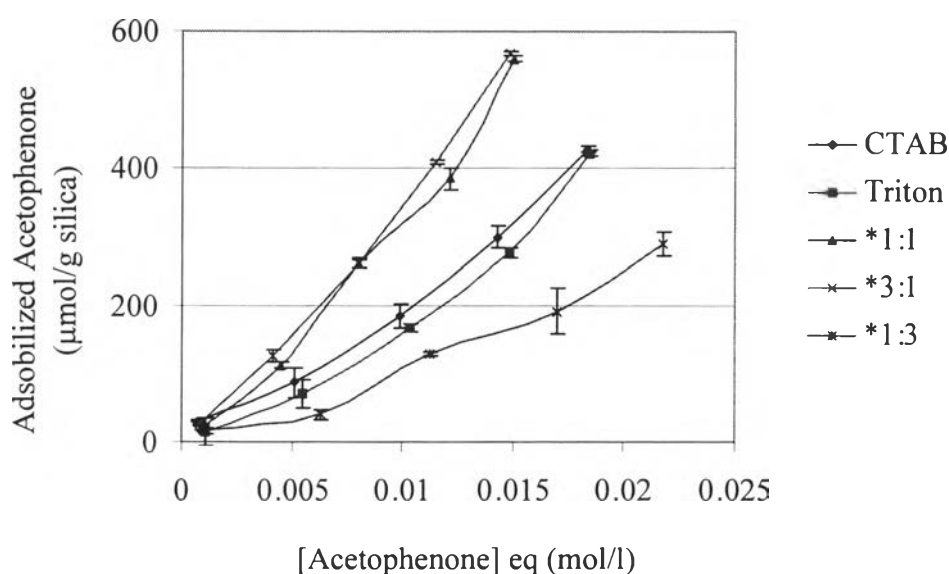
**Figure 4.6** Partition coefficient (K) of toluene adsorption at pH 8 (\*denotes CTAB).

#### 4.2.1.2 Adsorption of Acetophenone

The adsorption of acetophenone was investigated by using a similar approach as for the adsorption of toluene. The amount of acetophenone remaining in the supernatant was measured by UV-VIS spectrophotometer (245 nm).

Figure 4.7 shows the adsorption isotherms of acetophenone, which are the plot between the adsorbed amounts of acetophenone versus the equilibrium concentration of acetophenone in the aqueous phase at pH 8. The adsorption of acetophenone increases with increasing equilibrium concentration of acetophenone. In single system, it is interesting to see that acetophenone adsorption for both CTAB and Triton are quite similar despite much difference in the amount of surfactant adsorbed on silica (700  $\mu\text{mol/g}$

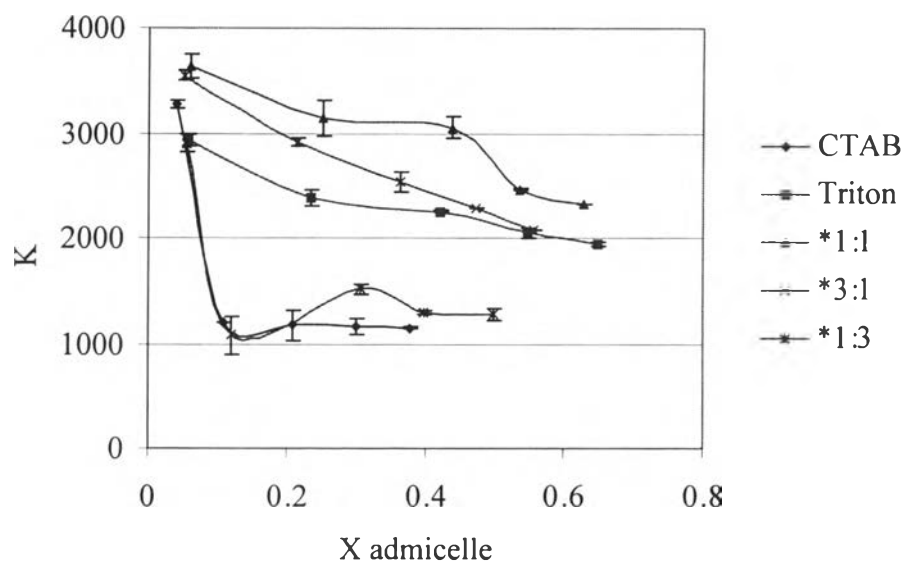
for CTAB and 230  $\mu\text{mol/g}$  for Triton). In mixed surfactant system, it is obvious that the presence of Triton in the mixed system has synergistic effect on the adsolubilization of acetophenone, which can be attributed to the EO group of Triton. At CTAB:Triton molar ratio of 3:1, the acetophenone adsolubilization is almost twice of the adsolubilization in the system with CTAB alone despite much lower amount of surfactant adsorbed on silica.



**Figure 4.7** Adsolubilization of acetophenone in various surfactant systems at pH 8 (\*denotes CTAB).

Figure 4.8 is the plot of the partition coefficient ( $K$ ) versus the mole fraction of acetophenone in the admicelle. In case of CTAB and mixed CTAB/Triton ratio 1:3, the partition coefficient dramatically decreases in the low  $X_{\text{admicelle}}$  range and then becomes constant, but for Triton, mixed CTAB/Triton ratio 1:1 and 3:1 the partition gradually decreases and become constant. The adsolubilization behavior observed here can be attributed to a highly polar in nature of acetophenone, whose dipole moment is 10 times higher than toluene, and thus, it is expected that acetophenone adsolubilizes primarily into the head group and palisade region of the admicelle (Kitiyanan *et al.*, 1996; Kanjanakhunthakul, 2002; Asvapathanagul, 2003; Pradubmook *et al.*, 2003).



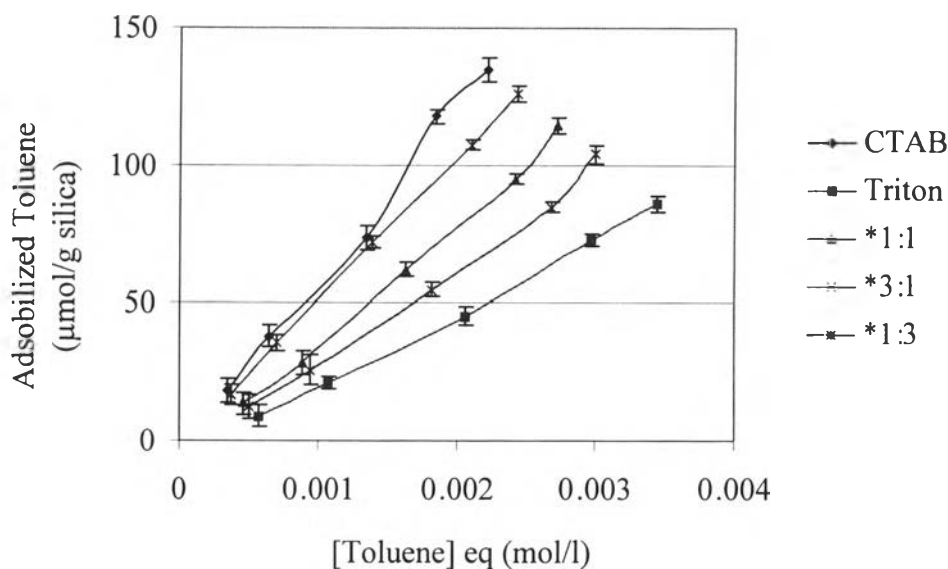


**Figure 4.8** Partition coefficient (K) of acetophenone adsolubilization at pH 8 (\*denotes CTAB).

#### 4.2.2 Mixed-Solute Systems

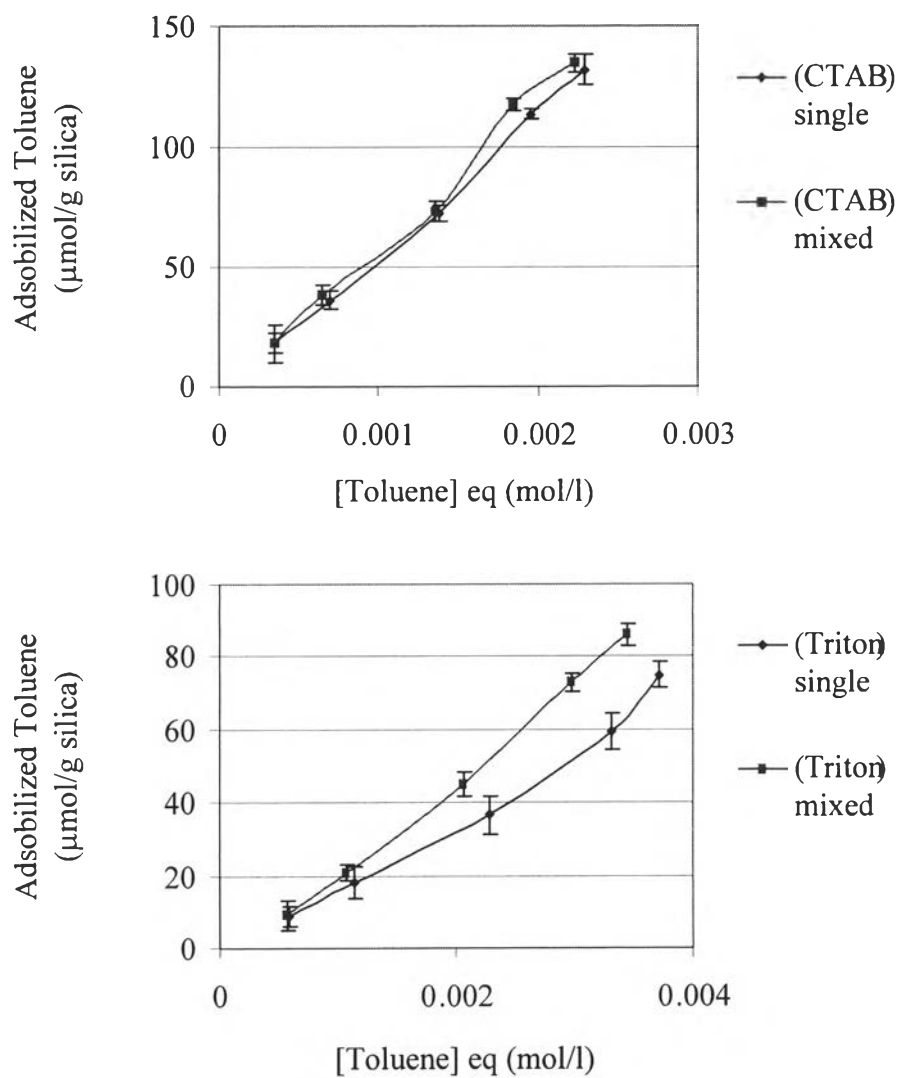
##### 4.2.2.1 *Adsolubilization of Toluene in the Presence of Acetophenone*

Figure 4.9 shows the plots of toluene adsolubilization versus equilibrium concentration of toluene in the presence of added acetophenone (0.87 mM) for both single- and mixed-surfactant system. In general, the adsolubilization of toluene increases with increasing equilibrium concentration of toluene. The adsolubilization of toluene in the presence of acetophenone for all surfactant systems show the same trend as the single-solute (pure) systems. In single surfactant system, adsolubilization of toluene is highest in the system of CTAB whereas the lowest is observed in the system having Triton alone. In the mixed surfactant system, adsolubilization is lowered with an increase in Triton content in the initial mixture.

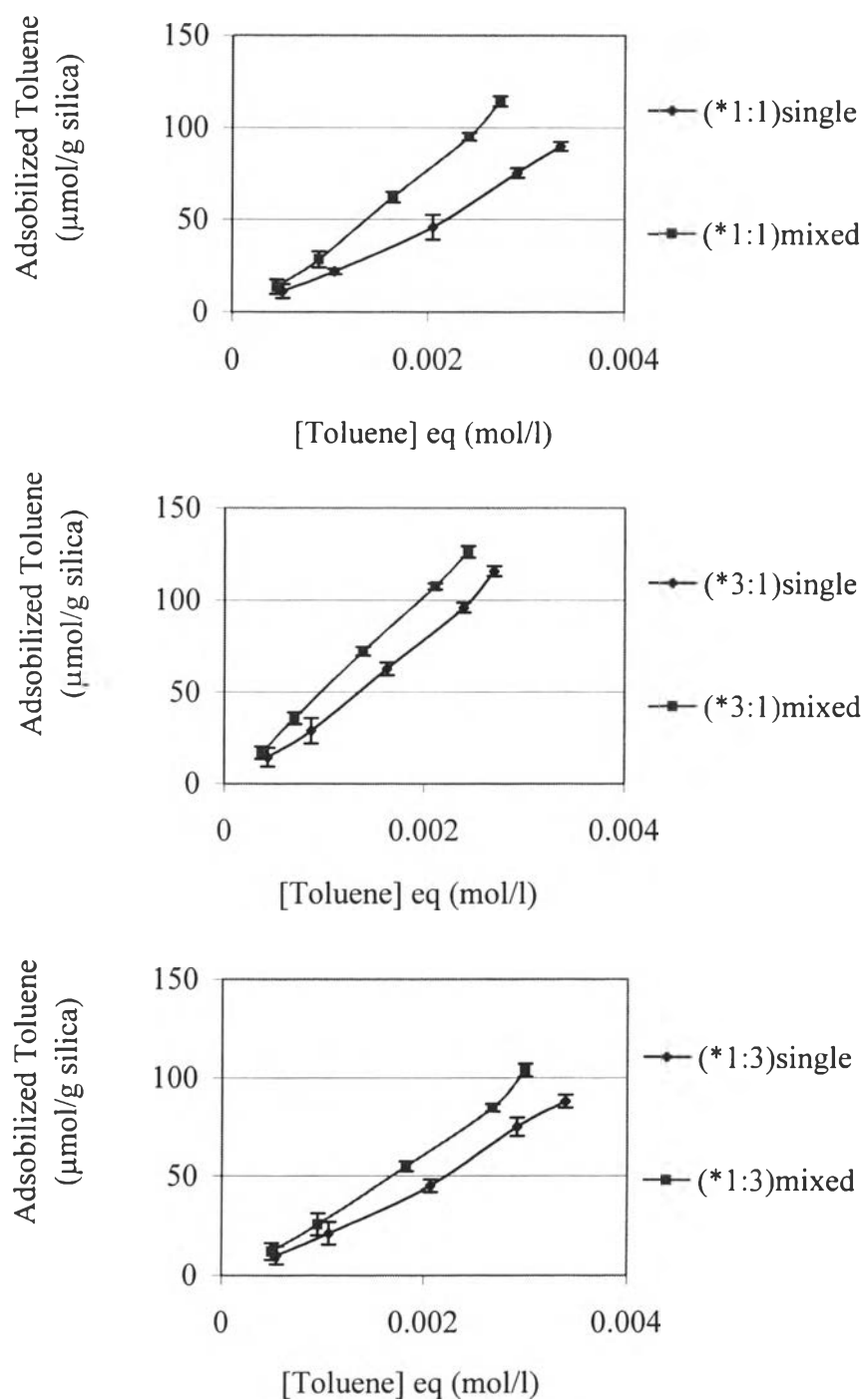


**Figure 4.9** Adsolubilization of toluene in the presence of acetophenone in various surfactant systems at pH 8 (\*denotes CTAB).

Figures 4.10 and 4.11 show the comparison of adsolubilization of toluene in the presence of acetophenone with toluene adsolubilization in the single-solute system for single- and mixed-surfactant systems, respectively. In CTAB system, slightly higher adsolubilization of toluene is observed in the presence of acetophenone as compared to the pure toluene system. In Triton system, adsolubilization of toluene in the presence of acetophenone is obviously higher than that in the system having toluene alone. In mixed-surfactant systems, the adsolubilization of toluene in the presence of acetophenone is clearly higher than that in the system having toluene alone. One possible reason for this effect is that the presence of acetophenone in the palisade region, resulting in an increase in the core volume of the admicelle and thus more toluene can then be adsolubilized.



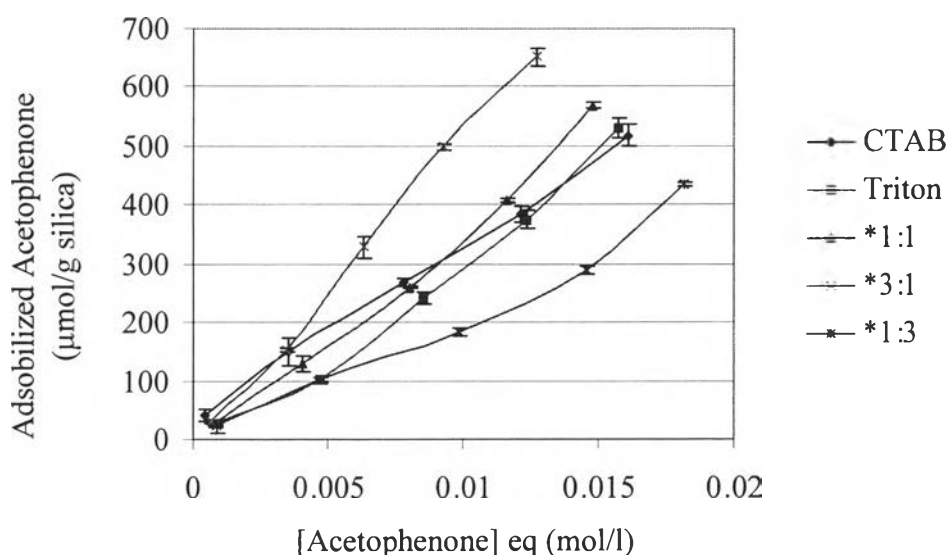
**Figure 4.10** Comparison of the adsolubilization of toluene in single-solute and mixed-solute systems in single surfactant system.



**Figure 4.11** Adsolubilization of toluene in the presence of acetophenone in mixed CTAB/Triton 1:1, 3:1 and 1:3 (\*denotes CTAB).

#### 4.2.2.2 Adsolubilization of Acetophenone in the Presence of Toluene

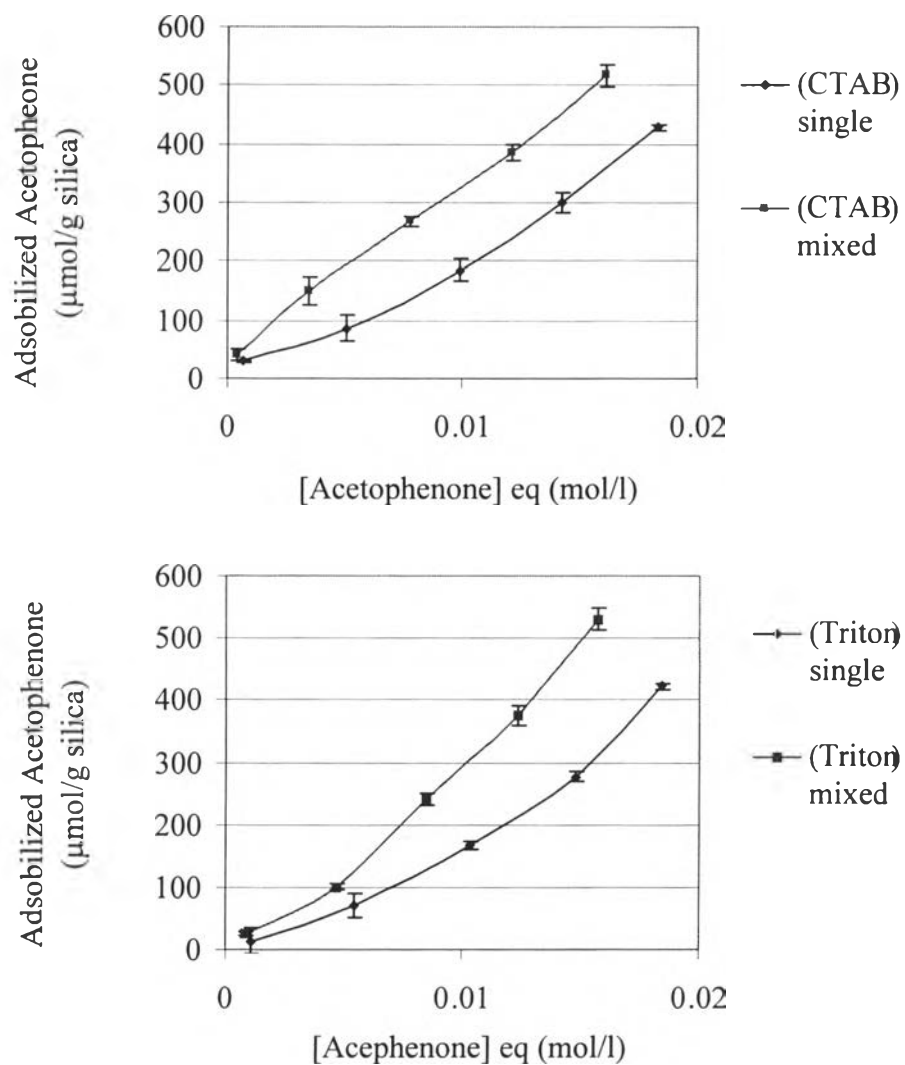
Figure 4.12 shows the plots of acetophenone adsolubilization versus equilibrium concentration of acetophenone in the presence of added toluene (5.59 mM) for both single- and mixed-surfactant system. In general, the adsolubilization of acetophenone increases with increasing equilibrium concentration of acetophenone. The synergistic effect has also been observed in the mixed CTAB/Triton at ratio 3:1 and 1:1 as in single-solute systems.



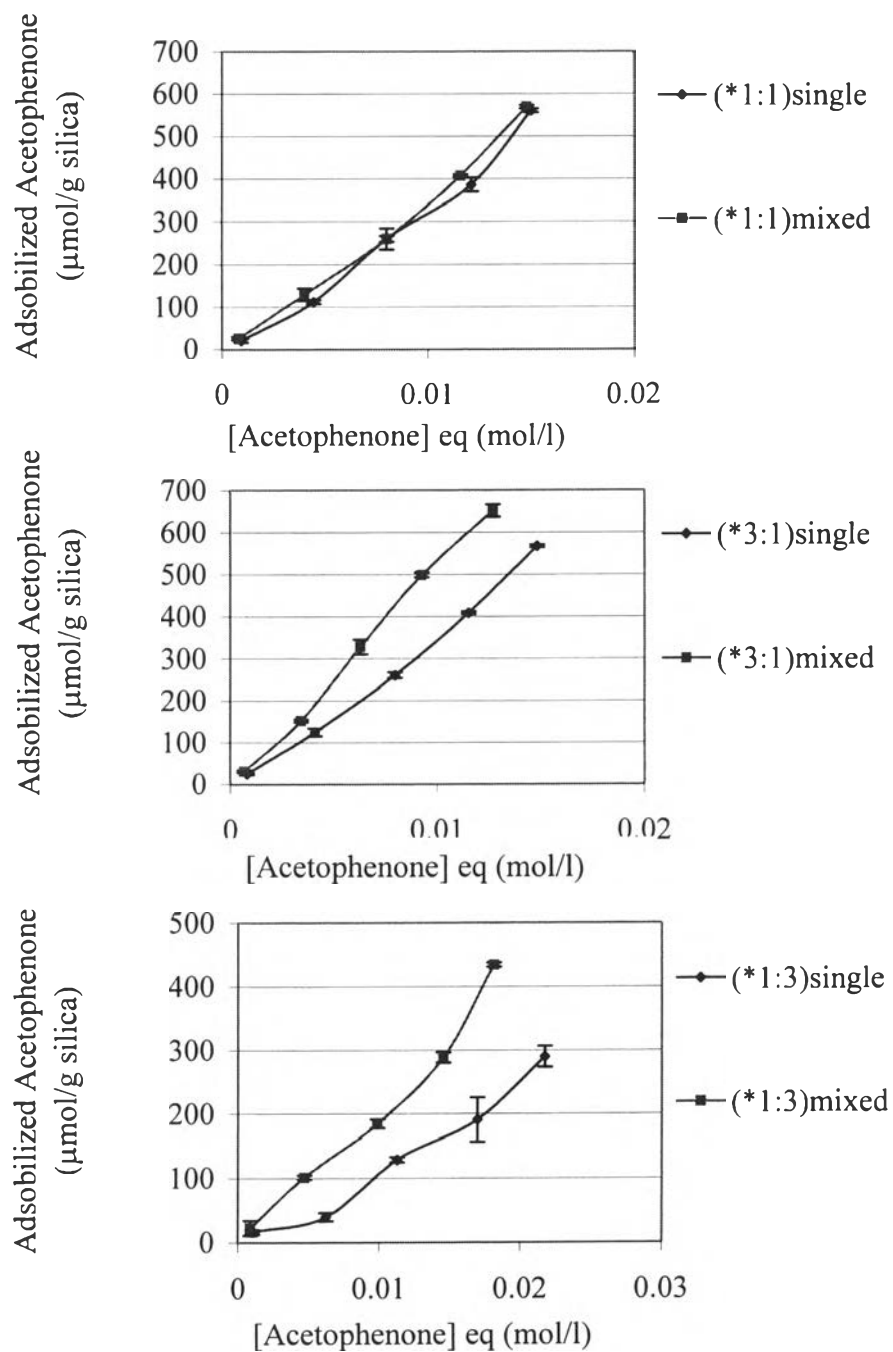
**Figure 4.12** Adsolubilization of acetophenone in the presence of toluene at pH 8 (\*denotes CTAB).

Figures 4.13 and 4.14 show the comparison of adsolubilization of acetophenone in the presence of toluene with acetophenone adsolubilization in the single-solute system for both single- and mixed-surfactant, respectively. In contrast to the toluene system, the acetophenone adsolubilization in the presence of toluene is noticeably higher than the acetophenone adsolubilization in single-solute system. Except for mixed CTAB/Triton at ratio 1:1, adsolubilization of acetophenone in mixed-solute system is slightly higher than that in single-solute system. This may be due to the highest packing of surfactant at this ratio as seen in the single-solute system. A possible explanation is that toluene in the core swells the bilayer loosening the molecules in the palisade layer, thus providing more volume for

acetophenone to adsorbilize. Additionally, the hydrophobic interaction between both adsorbilizates may also result in higher acetophenone adsorbilization in the presence of toluene (co-solute effect) (Kitiyanan *et al.*, 1996).



**Figure 4.13** Comparison of the adsorbilization of acetophenone in single-solute and the presence of toluene in single surfactant system.



**Figure 4.14** Adsolubilization of acetophenone in the presence of toluene in mixed CTAB/Triton 1:1, 3:1 and 1:3 (\*denotes CTAB).