



CHAPTER IV RESULTS AND DISCUSSION

4.1 Surfactant Adsorption

In this part of the study, the adsorption of CTAB, Triton X-165, and Triton X-305 on silica has been performed for single- and mixed-surfactant systems.

4.1.1 Single-Surfactant Systems

4.1.1.1 CTAB

Figure 4.1 shows the CTAB adsorption isotherm plotted on a log-log scale showing the regions II, III, and IV of the characteristic isotherm. It has been suggested that CTAB alone adsorbs appreciably on silica since silica surface is negatively charged, the electrostatic attraction with the cationic CTAB is dominant at low CTAB concentration. At high CTAB concentration, CTAB adsorbs through hydrocarbon chain-chain interaction with neighboring CTAB (Esumi *et al.*, 2001). From the plateau region, CTAB adsorption on silica is approximately 680 $\mu\text{mole/g}$. of silica. From Figure 4.1, the critical micelle concentration (CMC) of CTAB adsorbed on silica could be determined from the adsorption isotherm which is found to be approximately 800 μM .

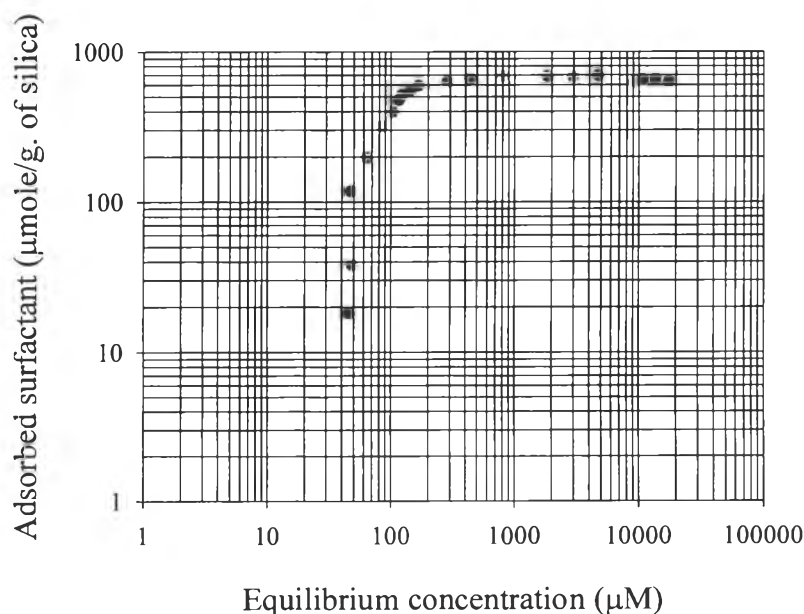


Figure 4.1 Adsorption isotherm of CTAB on Hi-Sil[®]255.

4.1.1.2 Triton X-165 and Triton X-305

Figures 4.2 and 4.3 show the adsorption isotherms of Triton X-165 and Triton X-305, plotted on a log-log scale. Both isotherms show the characteristic sigmoidal shape. From these two figures, the CMCs of Triton X-165 and Triton X-305 could be determined to be approximately 450 and 750 μM , respectively, which agrees well with the reported values (Factor *et al.*, 2001). The maximum surfactant adsorption on silica of Triton X-165 and Triton X-305 can be determined to be approximately 150 and 75 $\mu\text{mole/g.}$ of silica, respectively.

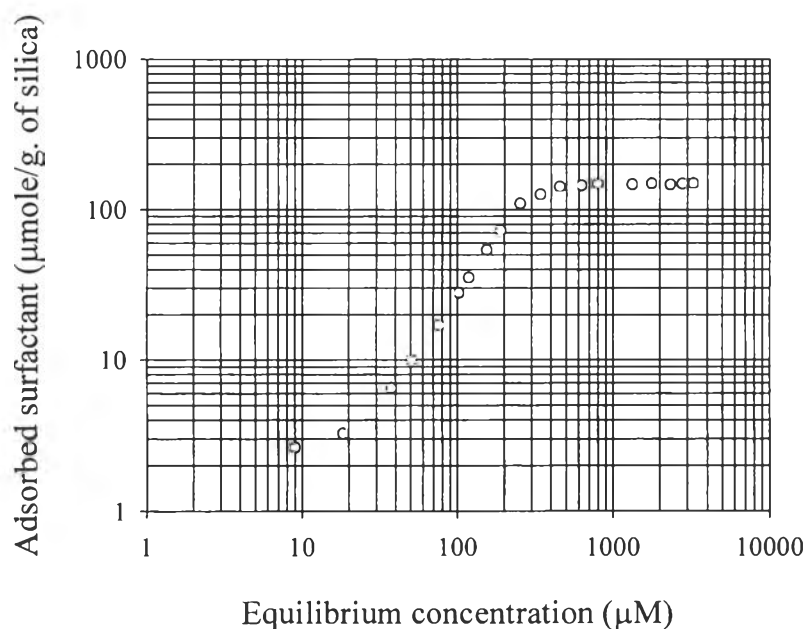


Figure 4.2 Adsorption isotherm of Triton X-165 on Hi-Sil[®]255.

Comparing the adsorption of CTAB and both Triton X-165 and Triton X-305, it can be noticed that CTAB adsorbs preferably on silica as indicated by a much higher adsorbed amount. This is attributed to the strong electrostatic interaction between cationic head groups of CTAB and negatively charged surface of silica.

In contrast, the driving force for the adsorption of nonionic surfactants such as Triton X-165 and Triton X-305 is supposed to be through hydrogen bonding rather than electrostatic interaction (Somasundaran, 1991). The

hydrogen bonding occurs between the ether oxygen of the surfactant and the surface hydroxyl groups of silica. In the low concentration region, the surfactant molecules lie flat on the silica surface. As adsorption increases, the flat hydrocarbon chain of Triton X- are considered to be perpendicular to the silica surface (Esumi *et al.*, 2001). From the plateau region, the maximum adsorption of Triton X-165 and Triton X-305 could also be determined which are approximately 150 and 75 $\mu\text{mole/g.}$ of silica, respectively. It can be seen that the maximum adsorbed amount decreases as the number of ethylene oxide groups increases. This is probably due to the repulsive interaction of hydrophilic heads between the already adsorbed molecules on the surface and the molecules going into the interface. Thus Triton X-305, having the number of ethylene oxide groups = 30, gives higher repulsion than Triton X-165, which has the number of ethylene oxide groups = 16, resulting in lower amount of adsorption (Jodar-Reyes *et al.*, 2002).

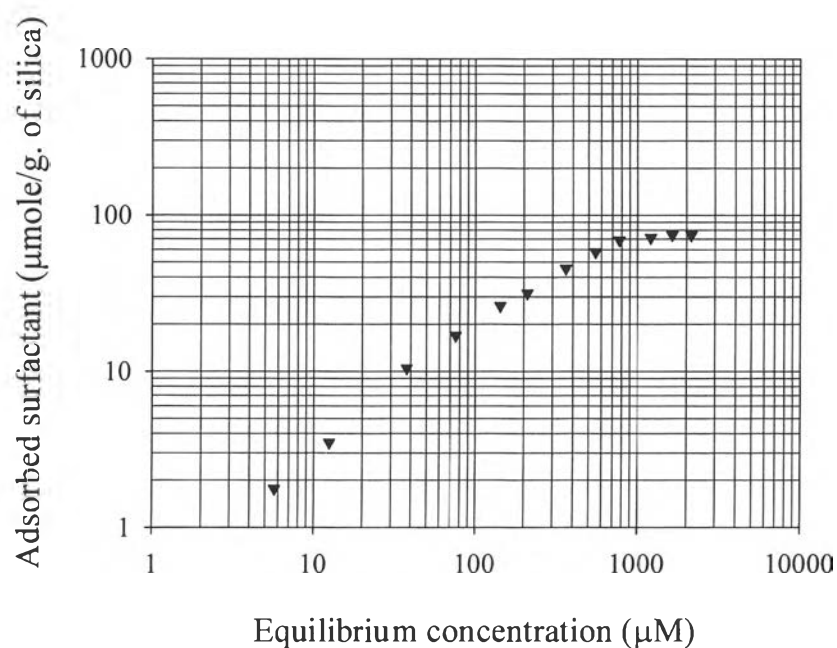


Figure 4.3 Adsorption isotherm of Triton X-305 on Hi-Sil[®]255.

4.1.2 Mixed-Surfactant Systems

For mixed-surfactant systems, the adsorption of CTAB and Triton X- mixtures was studied at the silica-water interface from the mixtures at several different initial molar ratios. The adsorption of surfactants can be presented in terms of total surfactant concentration (CTAB and Triton X-) and the concentration of each surfactant separately.

4.1.2.1 *CTAB: Triton X-165*

Figures 4.4, 4.5, and 4.6 show the adsorption isotherms of mixed CTAB and Triton X-165 at ratio 1:1, 3:1, and 1:3, presented as total surfactant concentration, CTAB concentration, and Triton X-165 concentration, respectively. From the isotherms, the CMC and maximum adsorption of the mixed-surfactant systems could be determined. It can be seen from Figure 4.4 that the addition of Triton X-165 into the systems causes a reduction in CMC of all three ratios. It is found that the mixed CTAB/Triton X-165 system having ratio 3:1 has the lowest CMC, which is approximately 300 μM whereas the systems having ratio 1:1 and 1:3, have CMC of approximately 500 and 600 μM , respectively. For the maximum surfactant adsorption, it is also seen that the adsorption of CTAB in the presence of Triton X-165 is lowered when compared with that of CTAB alone. Moreover, the decrease in the adsorption is proportional to the increase in the amount of Triton X-165 in the mixture. As seen in Figure 4.4, the maximum adsorption at ratio 3:1 is approximately 390 $\mu\text{mole/g}$. of silica, which is the highest, and also higher than the adsorption at ratios of 1:1 and 1:3, which are approximately 300 and 200 $\mu\text{mole/g}$. of silica, respectively. The decrease in the adsorption of CTAB upon addition of Triton X-165 is likely due to the competition between the bulky nonionic Triton X-165 and CTAB.

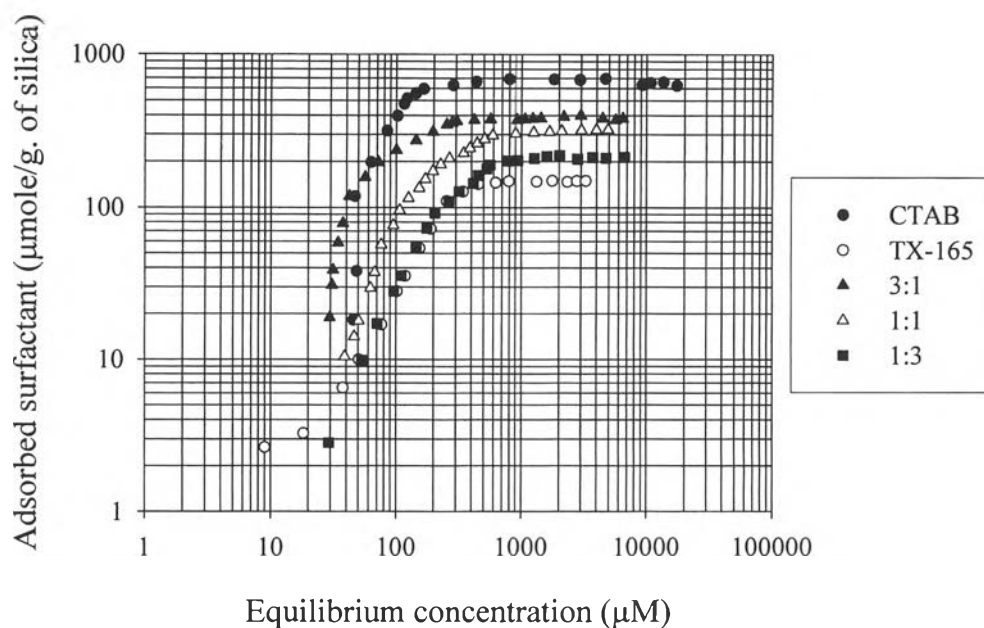


Figure 4.4 Adsorption isotherms of total surfactant in mixed CTAB: Triton X-165 adsorption on Hi-Sil[®]255 at various ratios.

For the individual surfactant adsorption from the mixture of CTAB and Triton X-165, it can be seen that the adsorption of CTAB from different mixtures with Triton X-165 is depressed when compared with that of CTAB alone as shown in Figure 4.5. The amount of CTAB adsorbed on silica decreases drastically with increasing molar ratio of Triton X-165 in the initial mixtures. As explained earlier, the decrease in the adsorption of CTAB upon addition of Triton X-165 is attributed to the competition between the bulky nonionic Triton X-165 and CTAB (Esumi *et al.*, 2001). In contrast, Triton X-165 adsorption is enhanced when CTAB is present in the mixture as the adsorption isotherms are shifted to lower surfactant concentration ranges as seen in Figure 4.6. It is suggested that the initial adsorption of CTAB through electrostatic interaction provides a number of hydrophobic sites that is sufficient to enable hydrophobic adsorption of Triton X-165.

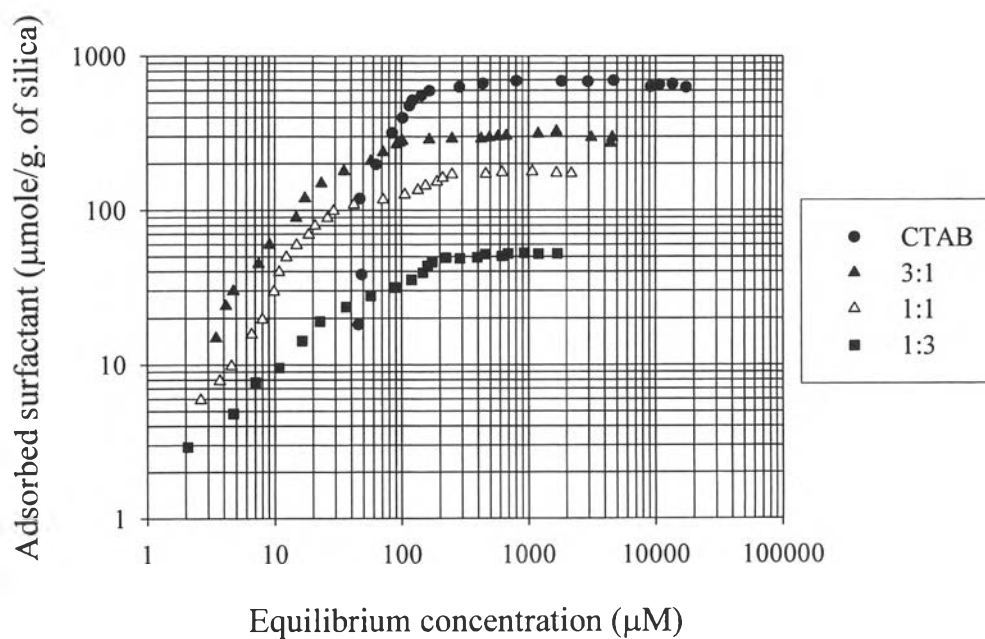


Figure 4.5 Adsorption isotherms of CTAB in mixed CTAB: Triton X-165 adsorption on Hi-Sil[®]255 at various ratios.

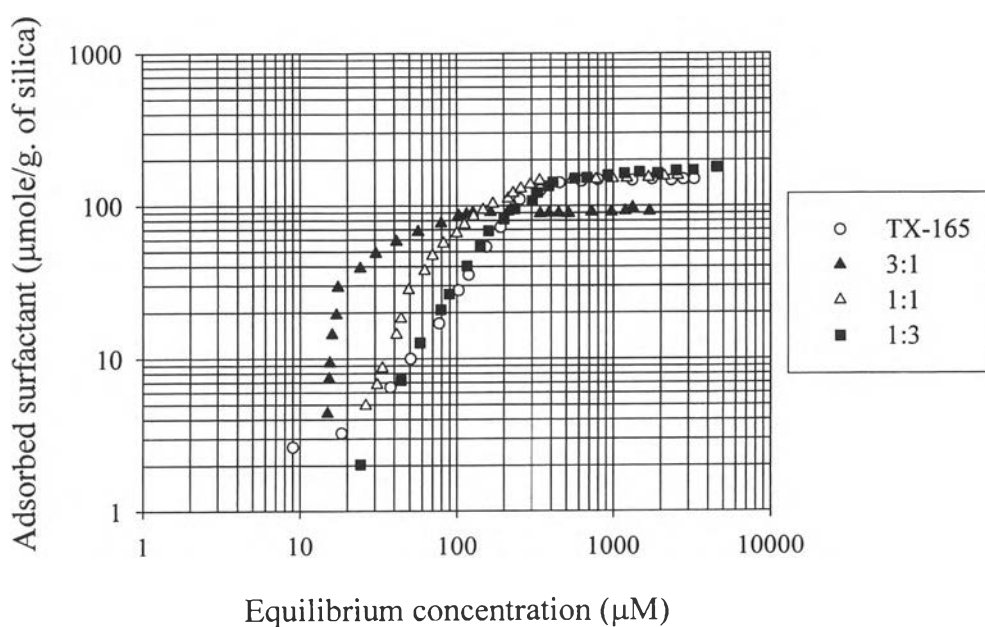


Figure 4.6 Adsorption isotherms of Triton X-165 in mixed CTAB: Triton X-165 adsorption on Hi-Sil[®]255 at various ratios.

4.1.2.2 CTAB: Triton X-305

Figures 4.7, 4.8, and 4.9 show the adsorption isotherms of mixed CTAB and Triton X-305 at ratio 1:1, 3:1, and 1:3, presented as total surfactant concentration, CTAB concentration, and Triton X-305 concentration, respectively. From the isotherms, the CMC of mixed CTAB and Triton X-305 adsorbed on silica could be determined. It can be seen from Figure 4.7 that the presence of Triton X-305 in the system causes an increase in CMC of the mixed-surfactant systems when compared with the single-surfactant system. The higher the molar ratio of Triton X-305 in the mixed-surfactant systems, the higher CMC is observed. It is found that ratio 3:1 provides the lowest CMC, which is approximately 1,000 μM and also lower than ratio 1:1 and 1:3, which CMC are approximately 1,500 and 1,800 μM , respectively. This is probably due to the barrier that comes from the very large area of head groups of Triton X-305.

For the amount of surfactant adsorption, similar results to those obtained in mixed CTAB and Triton X-165 systems are observed that is the addition of Triton X-305 causes lower adsorption of CTAB when compared with that of CTAB alone. Moreover, it is found that the adsorption of Triton X-305 at low concentration is enhanced by the coadsorption of CTAB. From the plateau region of each system, the highest adsorption is formed at ratio 3:1, which is approximately 300 $\mu\text{mole/g.}$ of silica, and also higher than those at ratio 1:1 and 1:3, which are approximately 170 and 100 $\mu\text{mole/g.}$ of silica, respectively. This result also suggests that the initial electrostatic adsorption of CTAB on silica surface plays an important role in providing hydrophobic sorption sites for the adsorption of Triton X-305. It is also observed that the adsorption of CTAB from different mixtures with Triton X-305 is depressed when compared with that of CTAB alone, suggesting that there might be the competition between CTAB and Triton X-305.

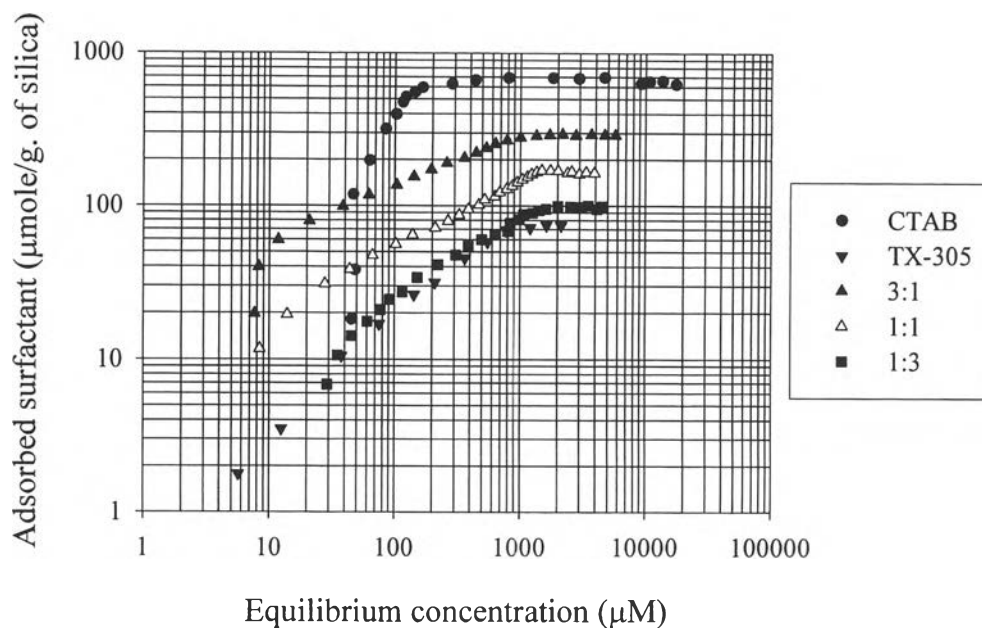


Figure 4.7 Adsorption isotherms of total surfactant in mixed CTAB: Triton X-305 adsorption on Hi-Sil[®]255 at various ratios.

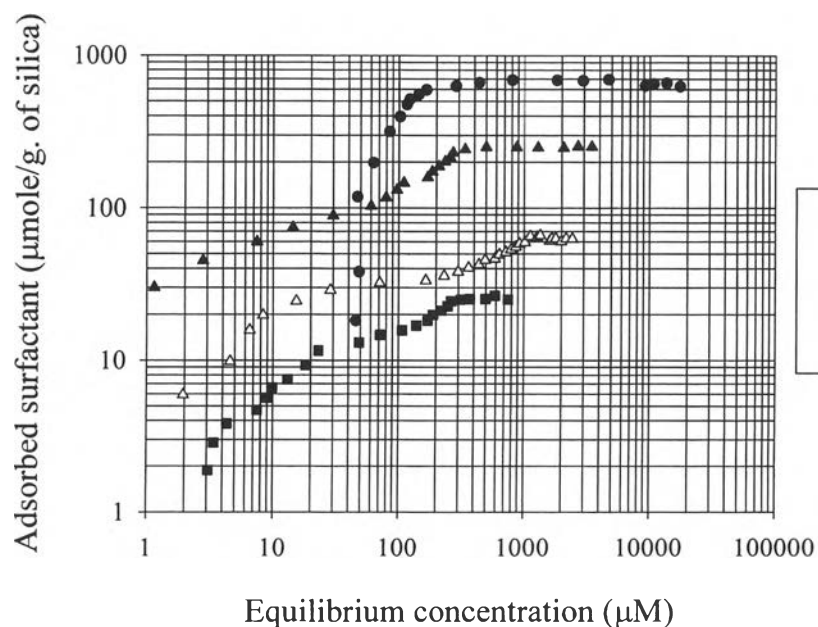


Figure 4.8 Adsorption isotherms of CTAB in mixed CTAB: Triton X-305 adsorption on Hi-Sil[®]255 at various ratios.

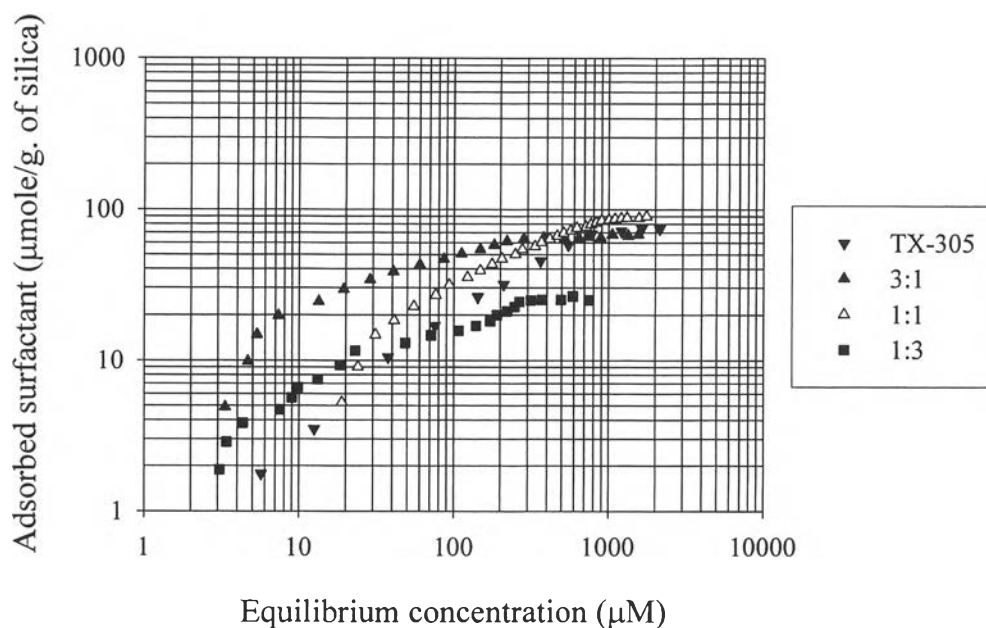


Figure 4.9 Adsorption isotherms of Triton X-305 in mixed CTAB: Triton X-305 adsorption on Hi-Sil[®]255 at various ratios.

4.2 Adsolubilization

Toluene and acetophenone were selected as model organic solutes to adsolubilize into adsorbed single- and mixed-surfactant admicelles on silica. First the equilibrium surfactant adsorption on silica was carried out at a previously determined equilibrium surfactant concentration in the aqueous solution. The organic solute was then added to the equilibrium system described above by syringe injection into the crimp-sealed vial.

4.2.1 Adsolubilization of Toluene

The adsolubilization behavior of surfactants adsorbed on silica surface for toluene was investigated in single- and mixed-surfactant systems. After equilibrium was achieved in the adsolubilization experiment described above, the concentration of toluene in the supernatant was analyzed by a headspace gas

chromatography and the amount of toluene adsolubilized was determined using method of difference.

Figure 4.10 shows the plot of toluene adsolubilization versus the bulk equilibrium concentration of toluene in the single-surfactant system of CTAB, Triton X-165, and Triton X-305. A general trend can be observed in all three surfactant systems that as the equilibrium toluene concentration increases, the amount of adsolubilized toluene increases. From the comparison between the adsolubilization of toluene in different surfactant systems, one can see that the amount of toluene adsolubilized in CTAB is much higher than in Triton X-165 and Triton X-305, respectively. The adsolubilized amount is quite related to the amount of surfactant adsorbed on silica which CTAB adsorbed the highest when compared to Triton X-165 and Triton X-305, respectively (Figures 4.1, 4.2, and 4.3). The results suggest that the adsolubilization of toluene can be related to the amount of surfactant adsorbed on silica.

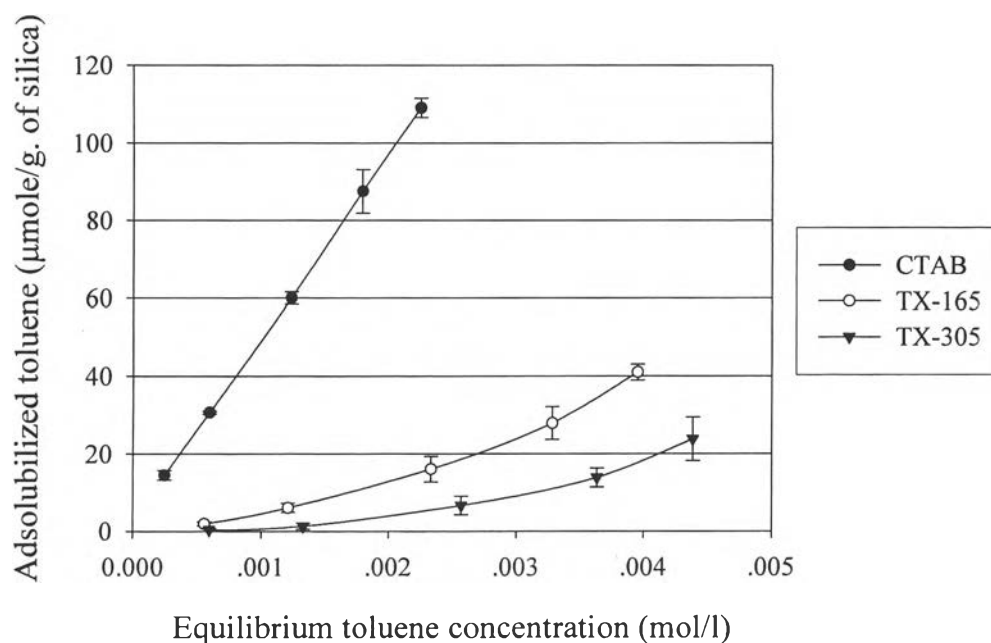


Figure 4.10 Adsolubilization isotherms of toluene in CTAB, Triton X-165, and Triton X-305.

Figure 4.11 shows the plot of toluene adsolubilization versus the bulk equilibrium concentration of toluene for mixed-surfactant system of CTAB and Triton X-165 at various molar ratios. From this figure, it can be seen that the toluene adsolubilization isotherms of the mixed-surfactant systems are in between those of CTAB and Triton X-165 pure systems. Similar to the adsolubilization behavior observed in the single-surfactant systems, the results suggest that the adsolubilization of toluene in the mixed-surfactant systems can also be related to the amount of surfactant adsorbed on silica. That is the adsolubilized amount corresponds well to the amount of surfactant adsorbed on silica as seen in Figure 4.4.

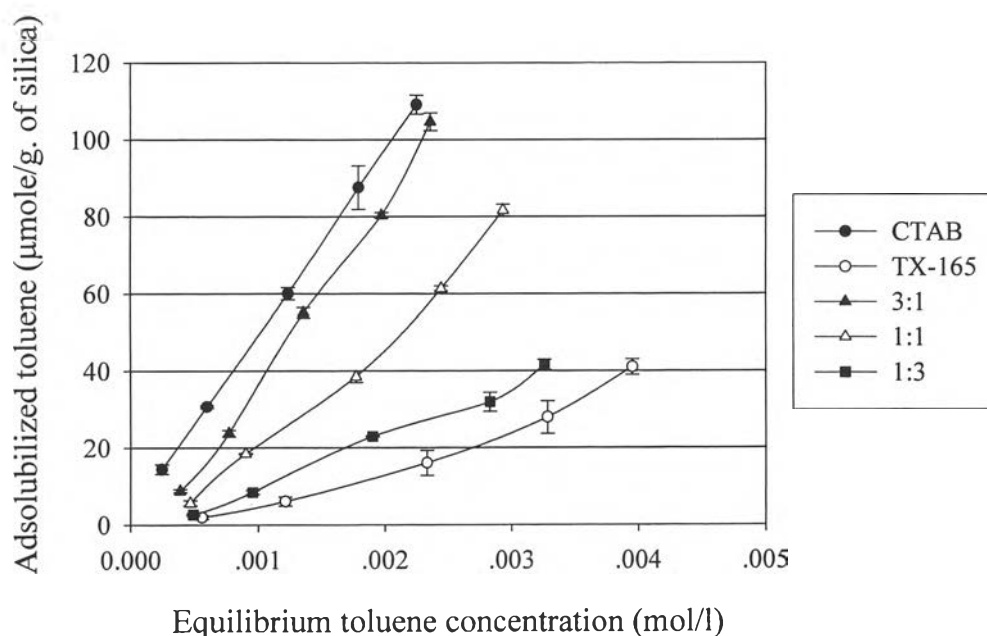


Figure 4.11 Adsolubilization isotherms of toluene in mixed-surfactant systems of CTAB and Triton X-165 at various ratios.

Figure 4.12 shows the plot of toluene adsolubilization versus the bulk equilibrium concentration of toluene for mixed-surfactant system of CTAB and Triton X-305 at various molar ratios. Generally, the results are similar to those observed in the mixed CTAB/Triton X-165 systems. The toluene adsolubilization isotherms of the mixed-surfactant systems are in the range between those of CTAB and Triton X-305 single systems. The results suggest that the adsolubilization of

toluene in mixed CTAB/Triton X-305 systems can be related to the amount of surfactant adsorbed on silica.

Comparing the mixed-surfactant systems of CTAB and Triton X-165 and CTAB and Triton X-305 (Figures 4.11 and 4.12), the amount of toluene adsolubilized in mixed-surfactant system of CTAB and Triton X-165 is higher than mixed-surfactant system of CTAB and Triton X-305 for all ratios. Once again, this can be attributed to the higher amount of surfactant adsorbed on silica in Triton X-165 systems than in Triton X-305 systems as seen in Figure 4.4 and Figure 4.7.

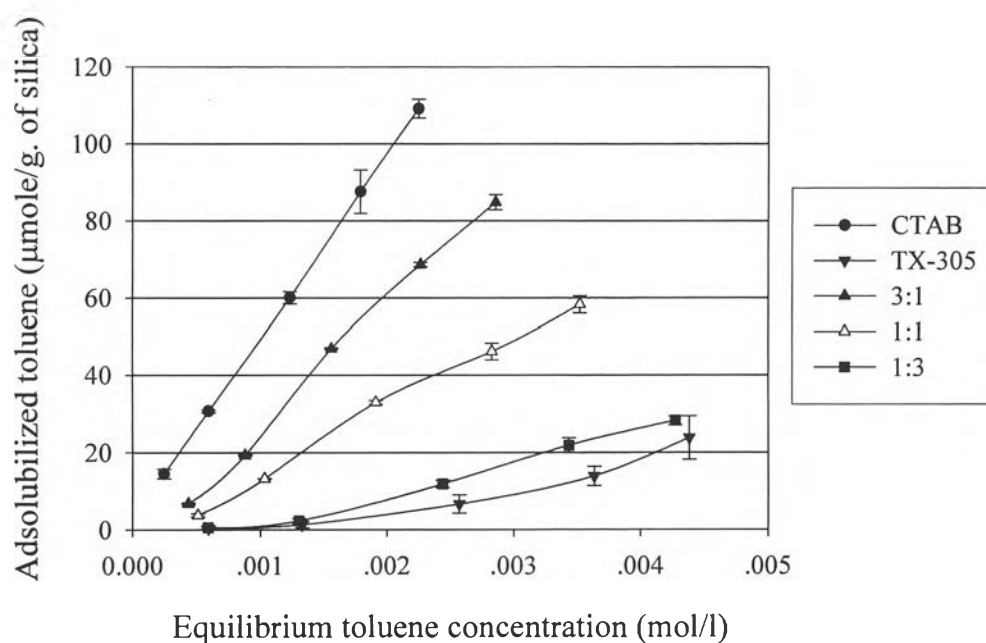


Figure 4.12 Adsolubilization isotherms of toluene in mixed-surfactant systems of CTAB and Triton X-305 at various ratios.

Figure 4.13 shows the plot of the partition coefficient (K) versus the mole fraction of toluene in the admicelle ($X_{\text{admicelle}}$) for CTAB, Triton X-165, and Triton X-305. It can be seen that initially the partition coefficient of toluene in CTAB decreases with increasing $X_{\text{admicelle}}$ and then becomes relatively constant. In contrast, the partition coefficients of toluene in Triton X-165 and Triton X-305 systems increase with increasing $X_{\text{admicelle}}$. This can be attributed to the properties of adsolubilize and the characteristics of the adsorbed surfactant on silica. Toluene is

a slightly polar organic solute and has been reported to solubilize into the palisade layer as well as the core of the admicelle (Kitiyanan *et al.*, 1996; Pradubmook *et al.*, 2003).

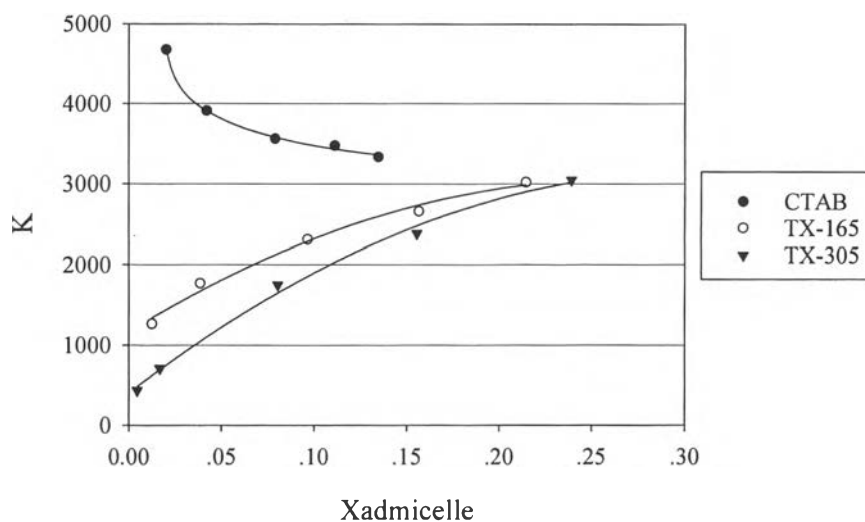


Figure 4.13 The Partition Coefficient (K) of toluene in CTAB, Triton X-165, and Triton X-305.

Figure 4.14 shows the plot of the partition coefficient (K) versus the mole fraction of toluene in the admicelle ($X_{\text{admicelle}}$) for mixed- surfactant system of CTAB and Triton X-165 at various molar ratios. It can be seen from this figure that for all three molar ratios the partition coefficient for toluene increase in the range of $X_{\text{admicelle}} = 0$ to 0.125 and then becomes quite constant in the range of $X_{\text{admicelle}} = 0.125$ to 0.2. Since toluene is a slightly polar organic solute, it is expected that toluene molecules would solubilize into the palisade layer as well as the core of the admicelle (Harwell, 1991). The partition coefficient of toluene in mixed- surfactant system of CTAB and Triton X-165 at ratio 3:1 is the highest and also higher than ratio 1:1 and 1:3, respectively. The results from the partition coefficient correspond well with the amount of adsorbed surfactant on silica. As the amount of surfactant adsorbed increases, the adsorption of surfactant on silica surface increases so does the core volume of the admicelle, resulting in higher toluene uptake as seen in Figure 4.11.

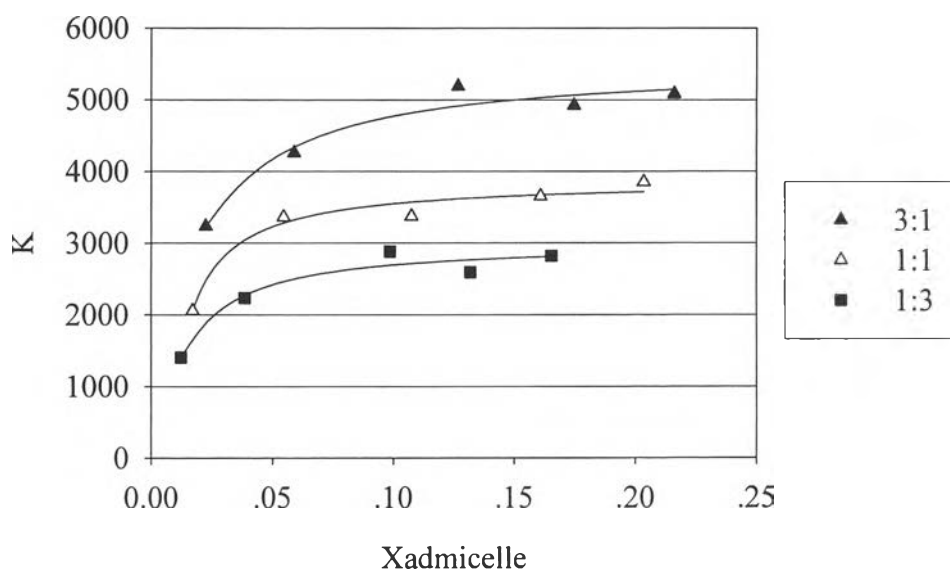


Figure 4.14 The Partition Coefficient (K) of toluene in mixed-surfactant systems of CTAB and Triton X-165 at various ratios.

Figure 4.15 shows the plot of the partition coefficient (K) versus the mole fraction of toluene in the admicelle ($X_{\text{admicelle}}$) for mixed-surfactant system of CTAB and Triton X-305 at various molar ratios. Similar results to those obtained in mixed-surfactant system of CTAB and Triton X-165 can be seen here where the partition coefficient of toluene in mixed-surfactant system of CTAB and Triton X-305 at ratio 3:1 is the highest and also higher than ratio 1:1 and 1:3, respectively. The partition coefficient of toluene adsolubilization for all three ratios increase in the range of $X_{\text{admicelle}} = 0$ to 0.15 and then becomes quite constant in the range of $X_{\text{admicelle}} = 0.15$ to 0.2 which can explain by the same reason described previously in the mixed-surfactant system of CTAB and Triton X-165.

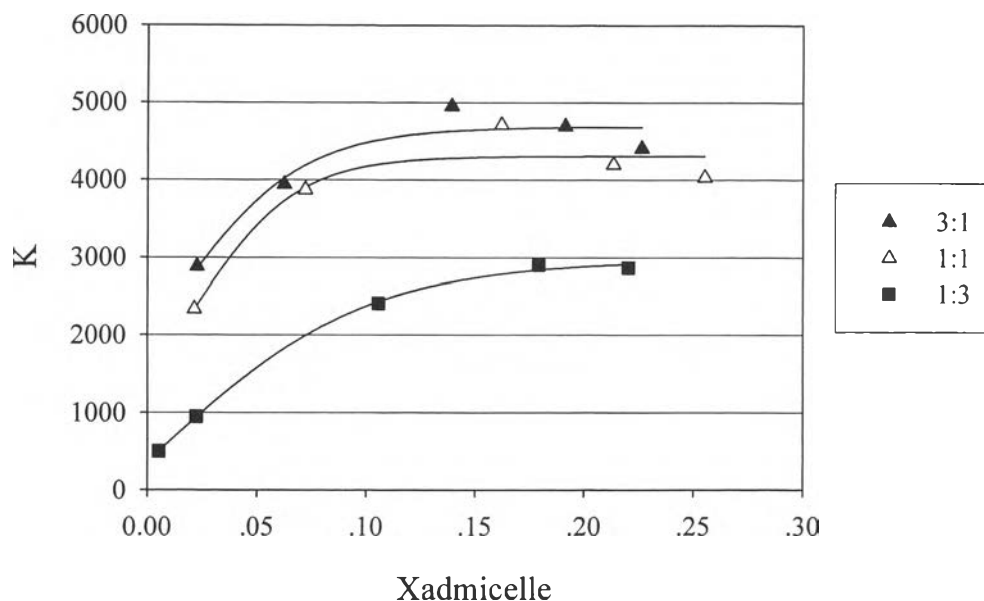


Figure 4.15 The Partition Coefficient (K) of toluene in mixed-surfactant systems of CTAB and Triton X-305 at various ratios.

4.2.2 Adsolubilization of Acetophenone

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

Figure 4.16 shows the plot of acetophenone adsolubilization versus the bulk equilibrium concentration of acetophenone for CTAB, Triton X-165, and Triton X-305. From this figure, a general trend can be observed that the adsolubilization of acetophenone increases with increasing equilibrium concentration of acetophenone for all three surfactant systems. It can be seen that the adsolubilization of acetophenone in Triton X-165 is higher than in CTAB and Triton X-305, respectively. It is important to note that this is not related to the amount of surfactant adsorbed on silica as observed in the case of toluene since Triton X-165 adsorbs to a much lesser extent than CTAB (Figures 4.1 and 4.2). This is probably due to the preference of acetophenone adsolubilized in the layer of surfactant adsorbed.

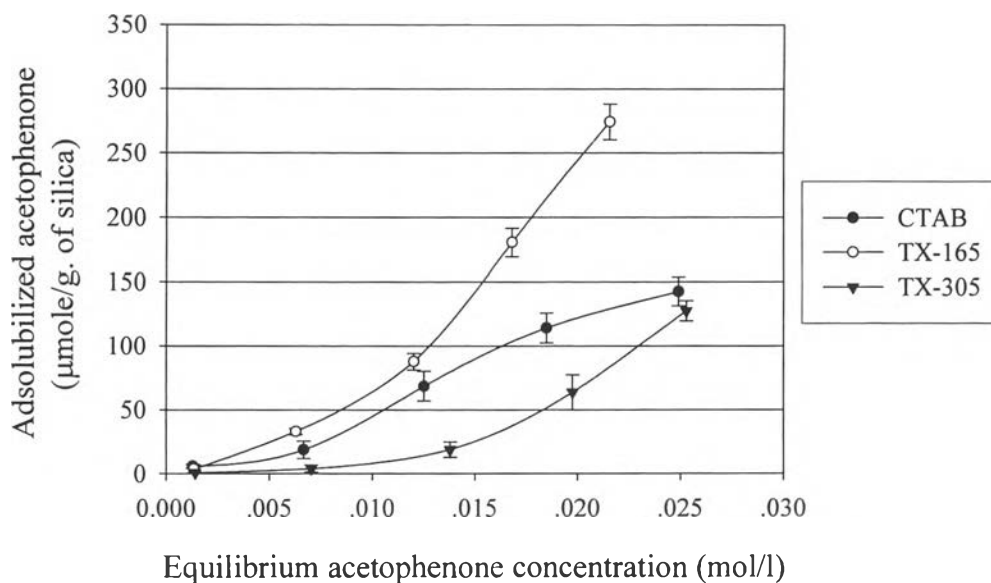


Figure 4.16 Adsolubilization isotherms of acetophenone in CTAB, Triton X-165, and Triton X-305.

Figures 4.17 and 4.18 show the plot of acetophenone adsolubilization versus the bulk equilibrium concentration of acetophenone for the mixed-surfactant systems of CTAB/Triton X-165 and CTAB/Triton X-305, respectively, at various molar ratios. It can be seen that the acetophenone adsolubilization of both mixed-surfactant systems for all ratios are higher than that of pure CTAB system, especially at the ratios of 3:1 and 1:1 where the amount of Triton X- is less than CTAB in the mixtures. For these two ratios, the amount of adsolubilized acetophenone is noticeably higher than in CTAB or Triton X- pure systems. For the ratio of 1:3, where the amount of Triton X- is greater than CTAB in the mixture, the adsolubilization of acetophenone is the lowest among the three ratios in both mixed-surfactant systems, yet still comparable to the pure systems of CTAB and Triton X-. The results clearly suggest that the incorporation of Triton X- into CTAB admicelles leads to synergistic behavior for the adsolubilization of acetophenone.

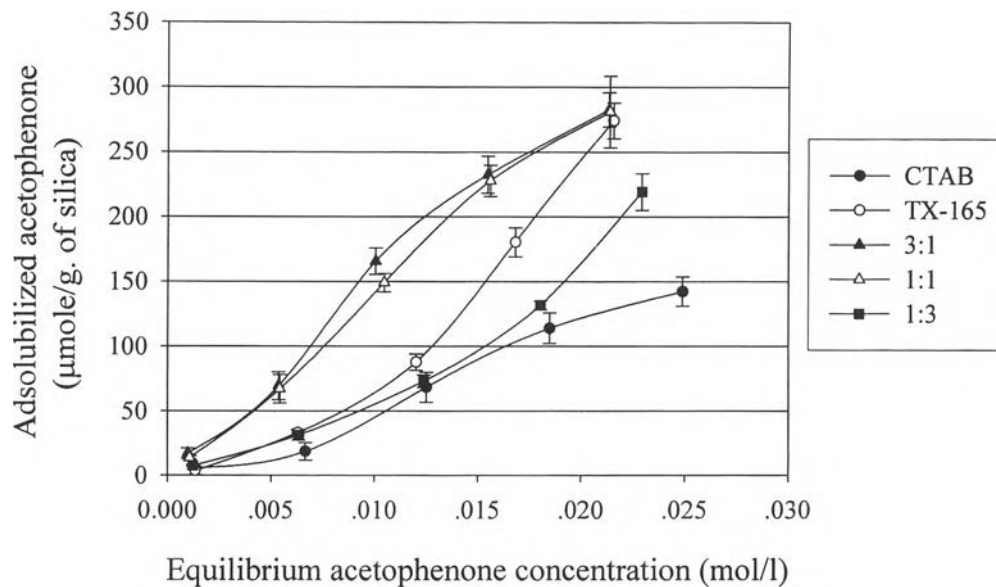


Figure 4.17 Adsolubilization isotherms of acetophenone in mixed CTAB:Triton X-165 systems at various ratios.

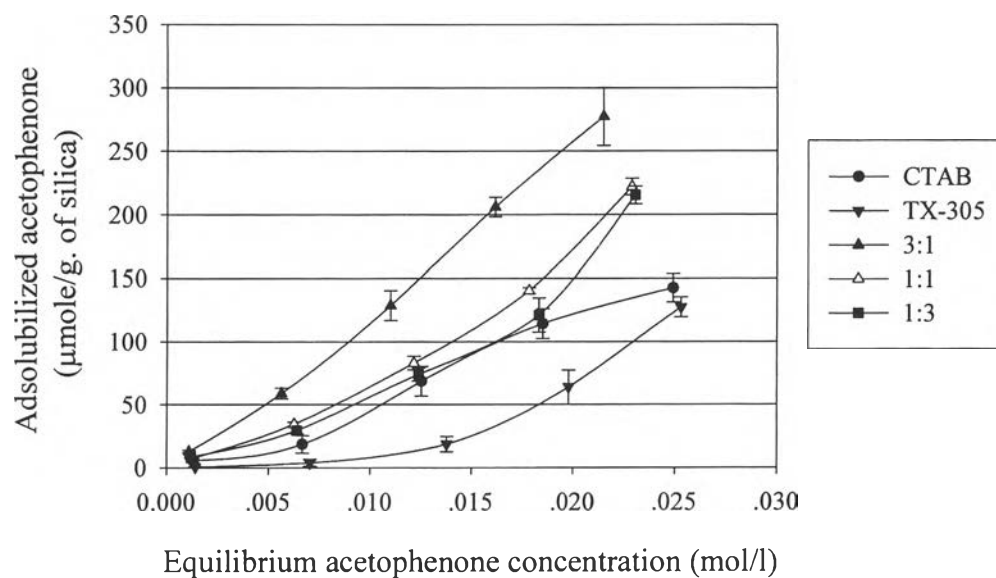


Figure 4.18 Adsolubilization isotherms of acetophenone in mixed CTAB:Triton X-305 systems at various ratios.

The plot between the partition coefficient (K) and the mole fraction of acetophenone in the admicelle ($X_{\text{admicelle}}$) in single surfactant systems is shown in Figure 4.19. It can be seen that the partition coefficient of CTAB decreases in the low $X_{\text{admicelle}}$ range and then become quite constant in the range of $X_{\text{admicelle}} = 0.08$ to 0.16 . Since acetophenone is a highly polar organic solute, it is expected that it adsorbilizes primarily into the head group and palisade regions of the admicelle (Rouse *et al.*, 1995). In contrast to CTAB, the acetophenone partition coefficient in Triton X-165 and Triton X-305 systems increases with increasing $X_{\text{admicelle}}$. This can be attributed to the bulky head groups present in the Triton X-165 and Triton X-305 systems which makes acetophenone adsorbilization difficult into the head group and palisade regions of the admicelles when compared to the CTAB system.

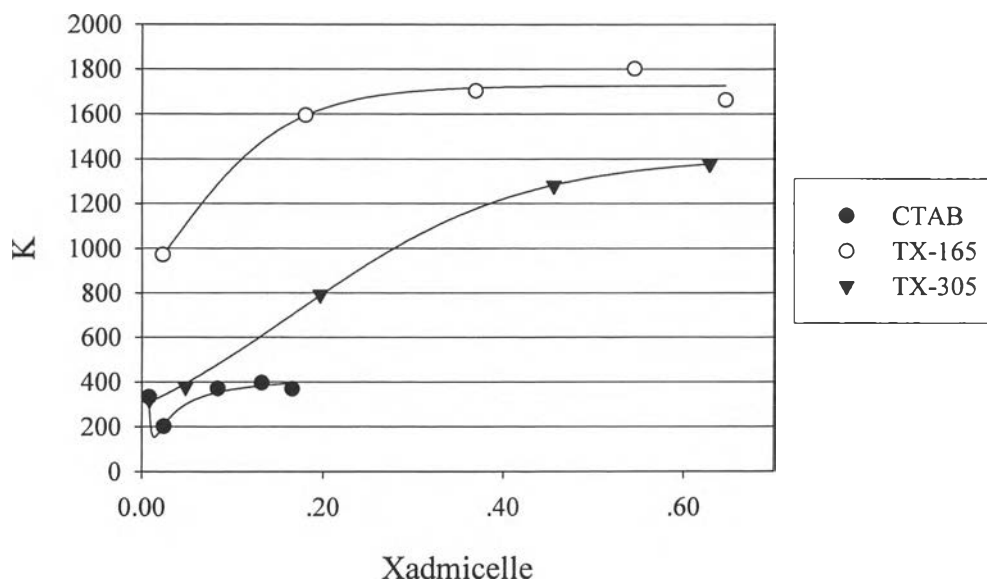


Figure 4.19 The Partition Coefficient (K) of acetophenone in single-surfactant system.

Figures 4.20 and 4.21 show the plots of the partition coefficient (K) versus the mole fraction of acetophenone in the admicelle ($X_{\text{admicelle}}$) in the mixed-surfactant systems of CTAB/Triton X-165 and CTAB/Triton X-305, respectively, at various molar ratios. It can be seen from these two figures that initially the partition

coefficient of acetophenone for all ratios decreases with increasing $X_{\text{admicelle}}$ and then becomes relatively constant. This synergism is interesting in that the partition coefficient in the pure Triton X- systems all increased, while in the mixed systems it always decreases. Thus, the presence of CTAB in the Triton X- admicelle competes for space in the polar head group / palisade regions, causing the partition coefficient to decrease.

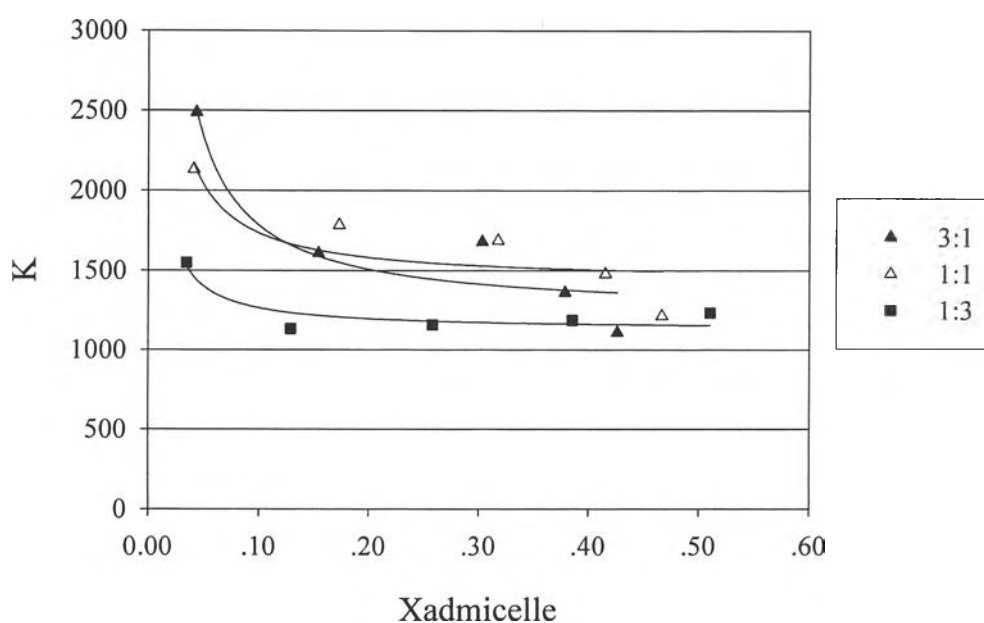


Figure 4.20 The Partition Coefficient (K) of acetophenone in mixed-surfactant systems of CTAB and Triton X-165 at various ratios.

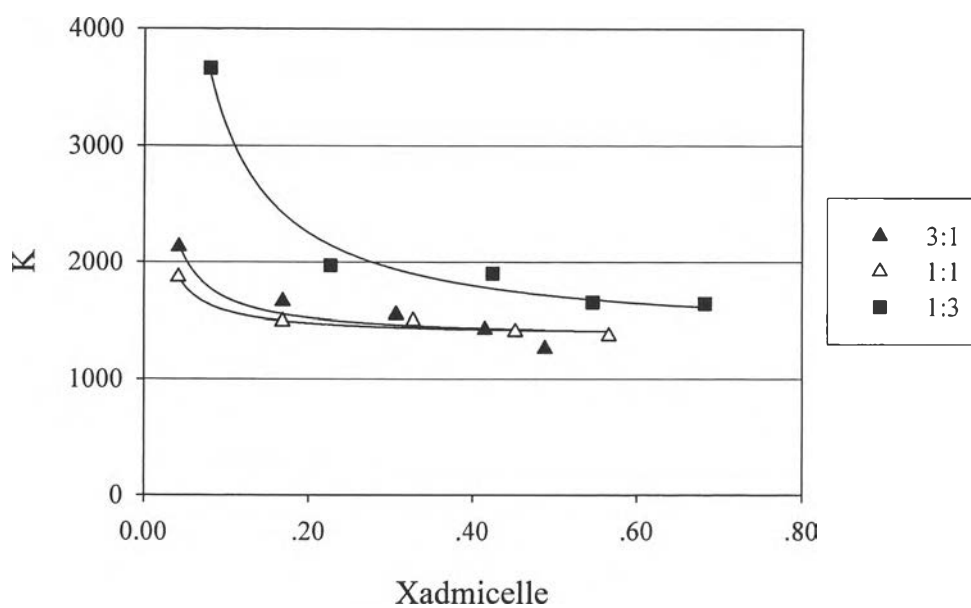


Figure 4.21 The Partition Coefficient (K) of acetophenone in mixed-surfactant systems of CTAB and Triton X-305 at various ratios.