

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Surfactant Adsorption

In this part of the study, the adsorption of single surfactants and mixed cationic-nonionic surfactants at various pH values on silica were studied.

4.1.1 Single-Surfactant Systems

4.1.1.1 *CTAB*

Figure 4.1 shows the adsorption isotherms of CTAB at pH 3, 5, and 8, plotted on a log-log scale. All of isotherms represent the characteristic regions II, III, and IV. From this figure, we can see that for every equilibrium concentration, CTAB adsorption on silica Hi-Sil[®]255 at pH 8 is always higher than the adsorption at pH 5 and pH 3. CTAB adsorption at pH 5 and pH 3 are similar though the amount adsorbed in region II of pH 5 is higher than that of pH 3. The critical micelle concentration (CMC) of CTAB adsorbed on silica at all pH values could be determined from the adsorption isotherms which are found to be approximately 900 μM , which agrees well with the reported value (Rosen, 1989). From the plateau region, it can be seen that the maximum CTAB adsorption on silica at pH 3 and pH 5 are nearly the same, approximately 480 $\mu\text{mol/g}$ silica, whereas at pH 8 CTAB adsorption plateaus at approximately 620 $\mu\text{mol/g}$ silica. This is expected and due to the fact that the surface of the silica becomes more negatively charged at pH higher than the point of zero charge (PZC) of silica, that is, a pH of 2-3. Thus, increasing pH of the system leads to higher amounts of head-on adsorbed surfactant on the silica (Holzheu *et al.*, 2000).

4.1.1.2 *Triton X-100*

Figure 4.2 shows the adsorption isotherms of Triton X-100 at pH 3, 5, and 8, plotted on a log-log scale. All the isotherms show the characteristic 'S' shape. As can be seen, Triton X-100 adsorption on silica Hi-Sil[®]255 at all three pH values is similar. However, in region II the adsorption of Triton X-100 at pH 8 is

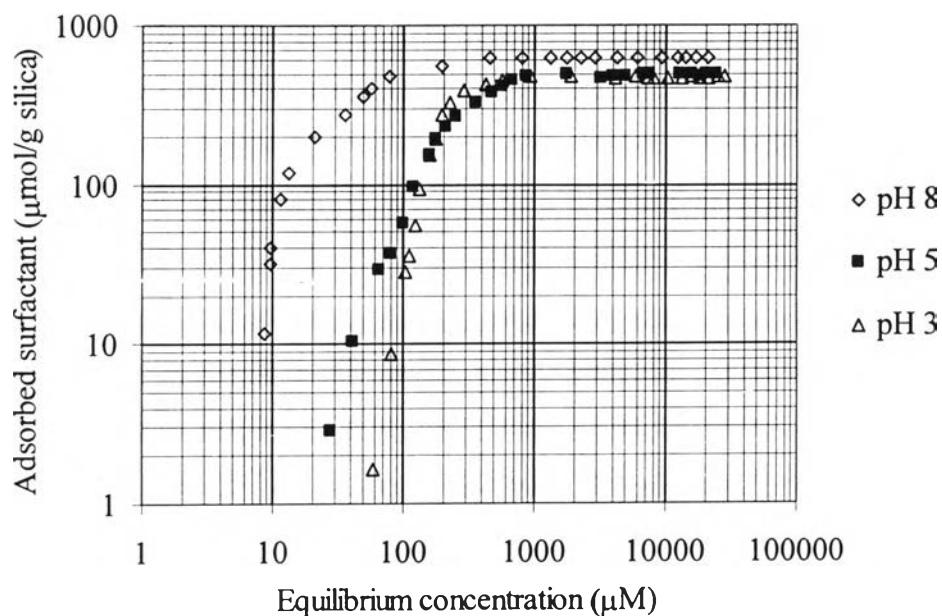


Figure 4.1 Adsorption isotherms of CTAB on Hi-Sil[®]255 at pH 3, 5, and 8.

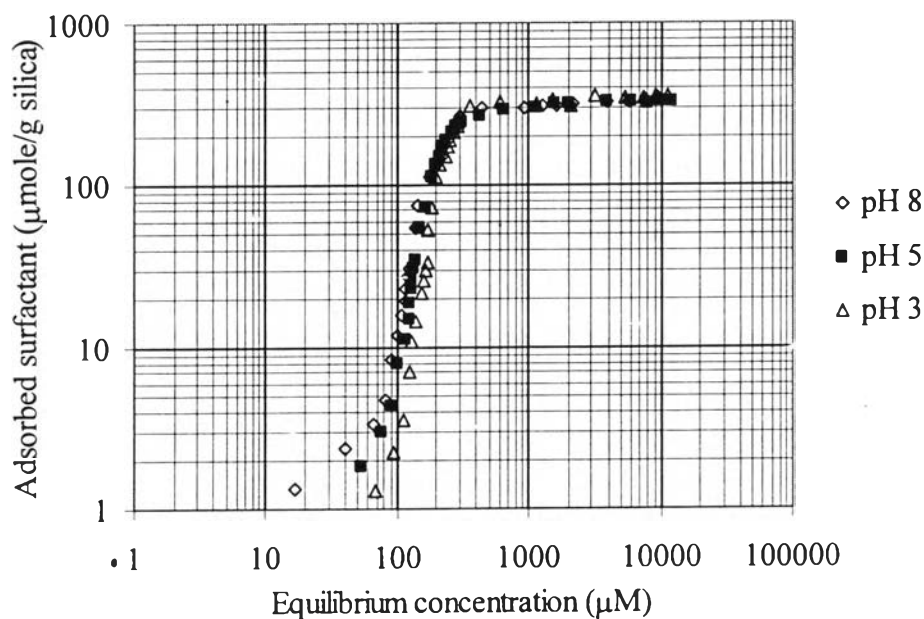


Figure 4.2 Adsorption isotherms of Triton X-100 on Hi-Sil[®]255 at pH 3, 5, and 8.

slightly higher than that at pH 5 and pH 3, respectively. The CMC of Triton X-100 adsorbed on silica at all pH values could be determined from the adsorption isotherm and were found to be approximately 300 μM , which agrees well with the reported

values (Huang and Gu, 1987). The maximum Triton X-100 adsorption on silica for all pH values is approximately 300 $\mu\text{mol/g}$ silica.

From these two figures, a comparison between the adsorption of CTAB and Triton X-100 can be made. It is obvious that CTAB adsorbs preferably on silica as indicated by a much higher adsorbed amount at all pH values. This strong interaction between the cationic surfactant and silica surface is electrostatically driven. At low CTAB concentrations, CTAB adsorbs on the silica surface by electrostatic attractive forces between its positively charged groups and negatively charged silica surface, orienting its hydrocarbon chain to the water phase. As CTAB concentration increases further, surfactant adsorbs through hydrocarbon chain-chain interaction with neighboring CTAB (Esumi *et al.*, 2001).

In contrast, the dominant interaction between nonionic surfactant and silica surface is hydrogen bonding (Penfold *et al.*, 2002). It is suggested that Triton X-100 molecules in the first layer are attached to the silica surface by their ethylene oxide chains such that hydrocarbon chains are exposed to water. As the concentration increases, the second layer forms on the surface. The surfactant molecules in the second layer are presumed to adsorb on those of the first in the opposite orientation, with the ethylene oxide chains directed toward the water phase (Huang and Gu, 1987). However, it can be seen from Figure 4.2 that pH has little effect on the adsorption of Triton X-100 on silica.

4.1.2 Mixed-Surfactant Systems

In this part of the study, the adsorption of mixed surfactants of CTAB and Triton X was studied at the silica-water interface from equimolar mixtures at various pH values. In the mixed CTAB/Triton system, TOC and UV-VIS spectrophotometer were systematically used to analyze the total surfactant concentration and Triton X-100 concentration, respectively. Then CTAB concentration was calculated by subtracting Triton X-100 concentrations from the total surfactant concentration. The results can thus be presented in terms of the total surfactant concentration (combined CTAB and Triton X-100) and the concentration of each surfactant separately.

4.1.2.1 Total Surfactant Adsorption

Figure 4.3 shows the total surfactant adsorption isotherms of the mixed surfactant systems at pH 3, 5, and 8, plotted on a log-log scale. The shape is intermediate between that of the ionic and nonionic surfactants alone, showing some linear regions but not particularly showing sharp boundaries or inflection points between regions. The CMC of the 1:1 mixed CTAB and Triton X-100 systems at the different pH values are quite close and in the range of 300-400 μM . These values correspond well to the result obtained from surface tension measurements. It can be seen that the addition of Triton X-100 causes a reduction in

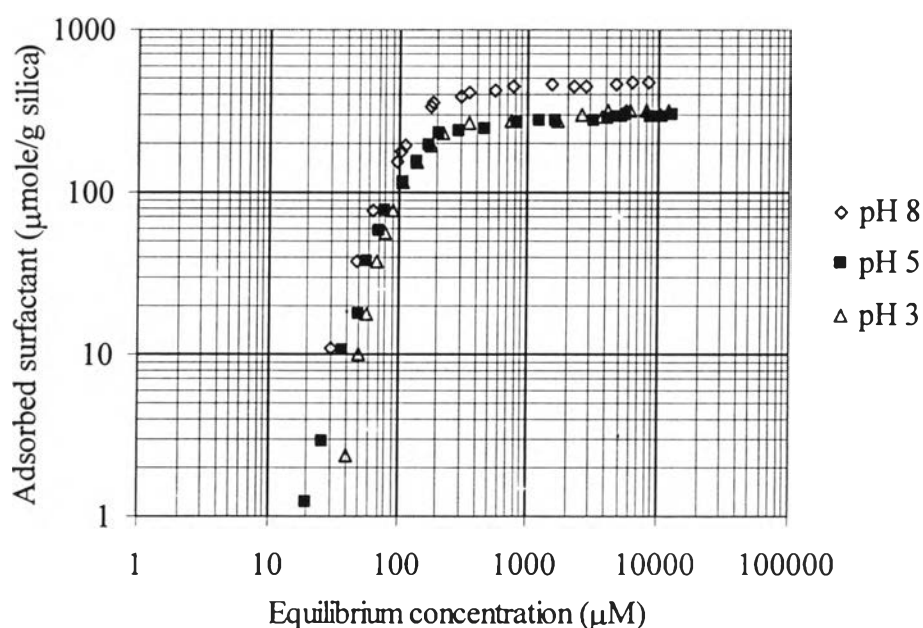


Figure 4.3 Adsorption isotherms of total surfactant in mixed CTAB/Triton X-100 adsorption on Hi-Sil[®]255 at pH 3, 5, and 8.

CMC of the system for all three pH values when compared to the pure CTAB systems. For the surfactant adsorption, the maximum adsorption at pH 3 and pH 5 are nearly the same, approximately 300 $\mu\text{mol/g silica}$, whereas at pH 8, the maximum surfactant adsorption on silica is higher (approximately 450 $\mu\text{mol/g silica}$). It is also found that an increase in pH has little effect on the actual amount of adsorption at low concentrations, though, for instance, at an equilibrium concentration of 40 micromolar, the adsorption at pH 5 is about 4 times that of pH 3.

The pH effect on the surfactant adsorption is more pronounced in the plateau regions. The higher surfactant adsorption at pH 8 than those at pH 5 and pH 3 suggests that increasing pH leads to higher amounts of head on adsorbed surfactant on the surface due to the higher surface charge.

It is also observed from the experiments that the ratio of the amount of each surfactant adsorbed onto precipitated silica is quite close to equimolar. That is, the surface concentration is similar to that of the feed at all pH values. For example, in mixed system of CTAB/Triton at pH 3, the adsorbed CTAB accounts for approximately 50% of the total adsorbed amount of surfactant and adsorbed Triton accounts for approximately 50% in the system.

4.1.2.2 CTAB Adsorption

Figure 4.4 shows the adsorption isotherms of CTAB on silica in both single- and mixed-surfactant systems at pH 3, 5, and 8, plotted on a log-log scale. All isotherms illustrate the characteristic regions II, III, IV.

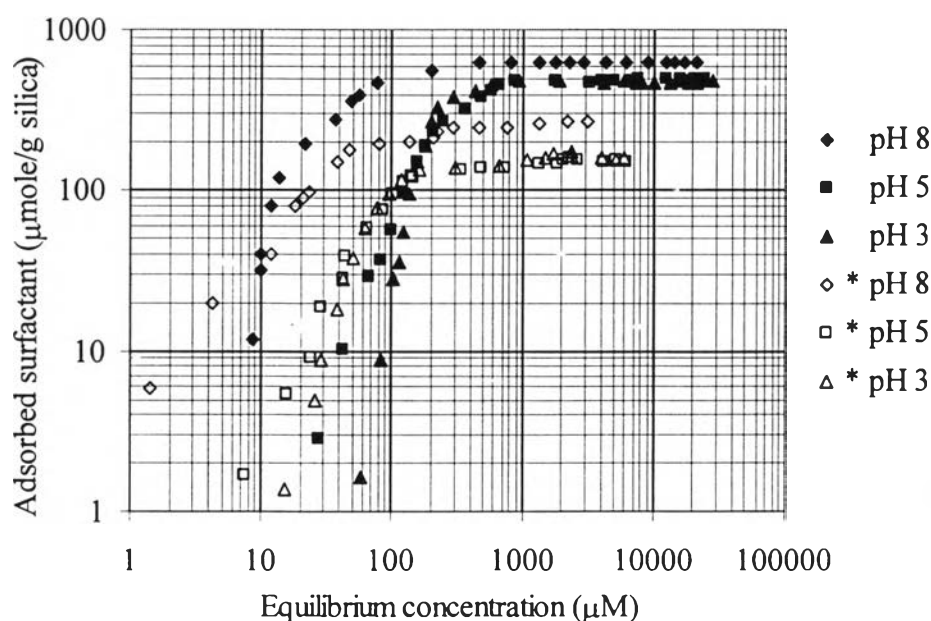


Figure 4.4 Adsorption isotherms of CTAB on Hi-Sil[®]255 in single system and mixed CTAB/Triton system at pH 3, 5, and 8, (*denotes mixed system).

In low concentration region, the adsorption of CTAB in mixed system is slightly enhanced by the addition of Triton in the system, whereas

the adsorption of CTAB in the plateau region decreases at all pH values in the presence of Triton. The decrease in the adsorption of CTAB in plateau region is due to the large volume taken up in the admicelle by the Triton molecule which does not allow tight packing of CTAB. It is also observed that in the plateau region the adsorption of CTAB in mixed system at pH 3 and pH 5 are quite close, which is similar to the adsorption of CTAB in single system.

4.1.2.3 Triton X-100 Adsorption

Figure 4.5 shows the adsorption isotherms of Triton on silica in single (pure) and mixed surfactant systems at pH 3, 5, and 8, plotted on a log-log scale. At low concentration region, the adsorption of Triton on silica surface is enhanced by the presence of CTAB. This may be explained by the strong adsorption of CTA^+ ions through electrostatic interactions which may then “attract” Triton X-100 molecules through hydrophobic interaction between their hydrocarbon chains. In the plateau region, the maximum adsorption of Triton in mixed system is lower than that in single system at all pH values. This is due to a lower packing density caused by the two, dissimilar surfactants.

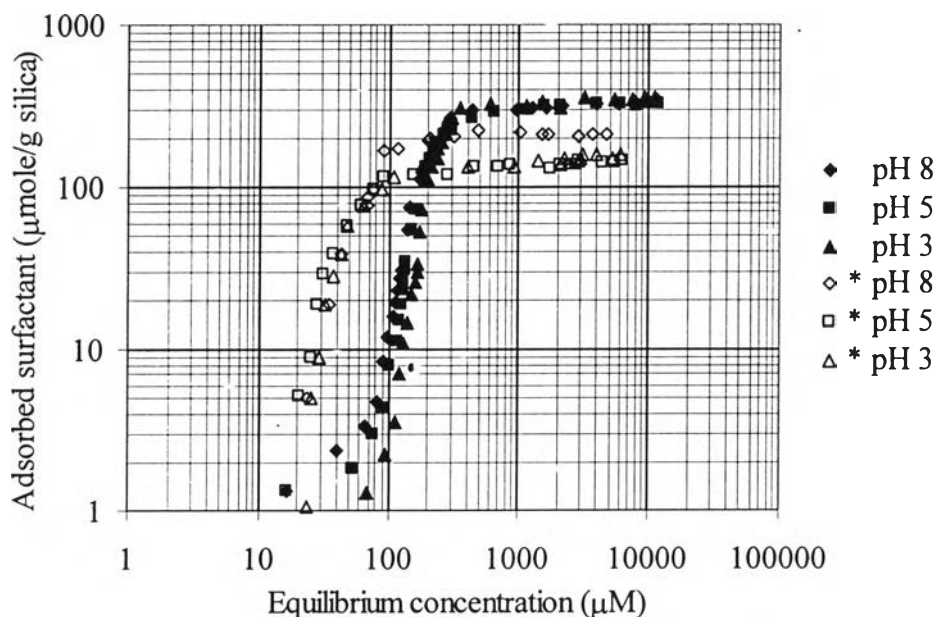


Figure 4.5 Adsorption isotherms of Triton X-100 on Hi-Sil[®]255 in single system and mixed CTAB/Triton system at pH 3, 5, and 8, (*denotes mixed system).

It is interesting to observe a difference between the pure Triton and mixed CTAB/Triton systems from this figure. That is, only in mixed system at higher equilibrium concentrations (higher than 90 μM) is the amount of adsorbed Triton X-100 at pH 8 is greater than that at pH 5 and pH 3. This might be due to an increase in the amount of CTAB which leads to the higher adsorption of Triton X-100.

4.2 Adsolubilization Studies

In this part of the study, the adsolubilization of three model organic compounds, benzene, toluene, and ethylbenzene, in the single- and mixed-surfactants systems of CTAB and Triton X-100 adsorbed on precipitated silica at pH 3, 5, and 8, were investigated. Adsorption isotherm data was used to determine a surfactant feed concentration that would equilibrate below the CMC of the surfactant system being studied. Organic solute was added to equilibrium surfactant/silica samples by syringe injections of varying amounts into the crimp-sealed vials, up to the water solubility of the solutes. The solubility of benzene, toluene, and ethylbenzene at 30°C are 1755 ppm, 542 ppm, and 165 ppm, respectively (Yaws, 1999). After appropriate equilibrium time, the concentration of the organic compound remaining in the supernatant was analyzed by a headspace gas chromatography and the amount of the organic compound adsolubilized was determined using a material balance.

4.2.1 Adsolubilization of Benzene

Figure 4.6 shows the adsolubilization isotherms of benzene at the three studied pH values. The adsolubilization of benzene increases with increasing equilibrium concentration of benzene for all systems. In single surfactant systems, the adsolubilization of benzene is the highest in the system of CTAB, whereas the lowest is observed in the system of Triton X-100 at all pH values. The results suggested that the adsolubilization of benzene may be related to the amount of adsorbed surfactant, and the amount of adsorbed CTAB is higher than that of Triton (Figures 4.1 and 4.2). When comparing the adsolubilization of benzene at three different pH values, it can be seen that the adsolubilization of benzene in both CTAB

and Triton systems at pH 8 is higher than that at pH 5 and pH 3 despite little difference in the amount of adsorbed surfactant on the silica at all pH values. This clearly indicates that the adsolubilization of benzene depends not only on the amount of adsorbed surfactant on silica but also on pH of the system. This can probably be attributed to the increase in the polarity of the surface at pH 8 which causes benzene, a polarizable organic solute, to have increased adsolubilization near the lower part of the admicelle, near the charged surface.

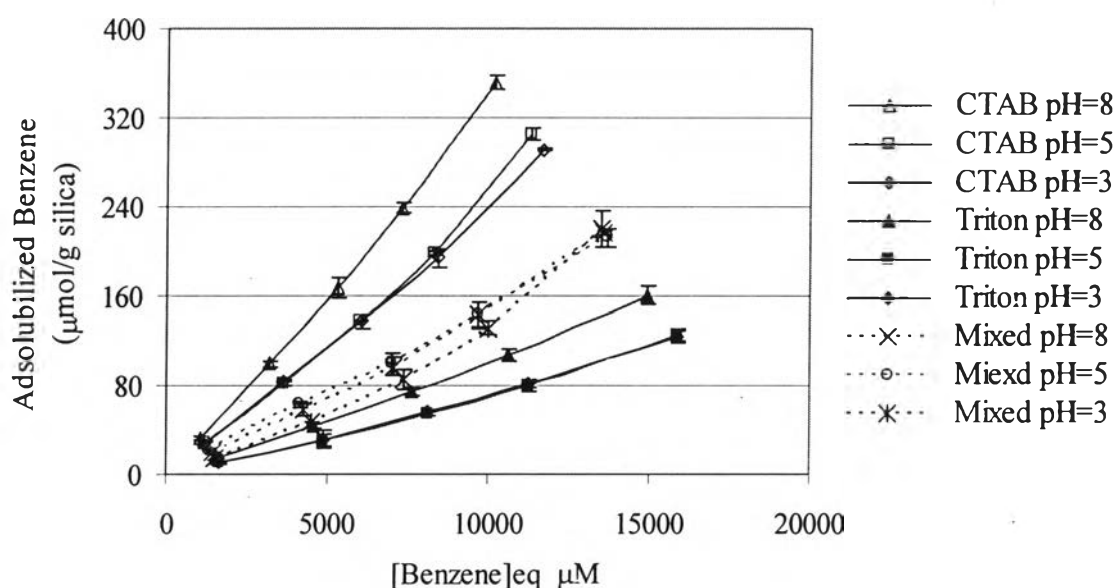


Figure 4.6 Adsolubilization of benzene in various surfactant systems at pH 3, 5, and 8.

In the mixed surfactant systems, compared to the CTAB-alone system, the presence of Triton results in lowered benzene adsolubilization. As previously seen in the surfactant adsorption studies, the addition of Triton causes the CMC of the mixed surfactant system to be lower as well as the amount of surfactant adsorbed. Thus, it can be expected that the benzene adsolubilization is lowered in the system with the addition of Triton. Comparing the pure Triton system and the mixed CTAB/Triton systems, although the amount of surfactant adsorbed in the two systems are quite similar, benzene adsolubilized is higher in the mixed CTAB/Triton system as seen in Figure 4.6. This may be due to the polarity and structure of the solute. Benzene is polar organic solute and has no attached branch and,

consequently, it can easily incorporate into the head and palisade regions of the admicelle. It can also be seen from the isotherms of the mixed surfactant systems that pH has little effect on benzene adsolubilization in the mixed surfactant system.

Figure 4.7 shows the value of the partition coefficient (K) versus the mole fraction of benzene in the admicelle ($X_{\text{admicelle}}$) at all pH values for CTAB, Triton, and mixed CTAB/Triton systems. The general trends observed in each plot are similar with the partition coefficient of benzene decreasing as the mole fraction of the benzene in admicelle increases. This is thought to indicate that the benzene partitions primarily into the palisade regions of the admicelle (Rouse *et al.*, 1995).

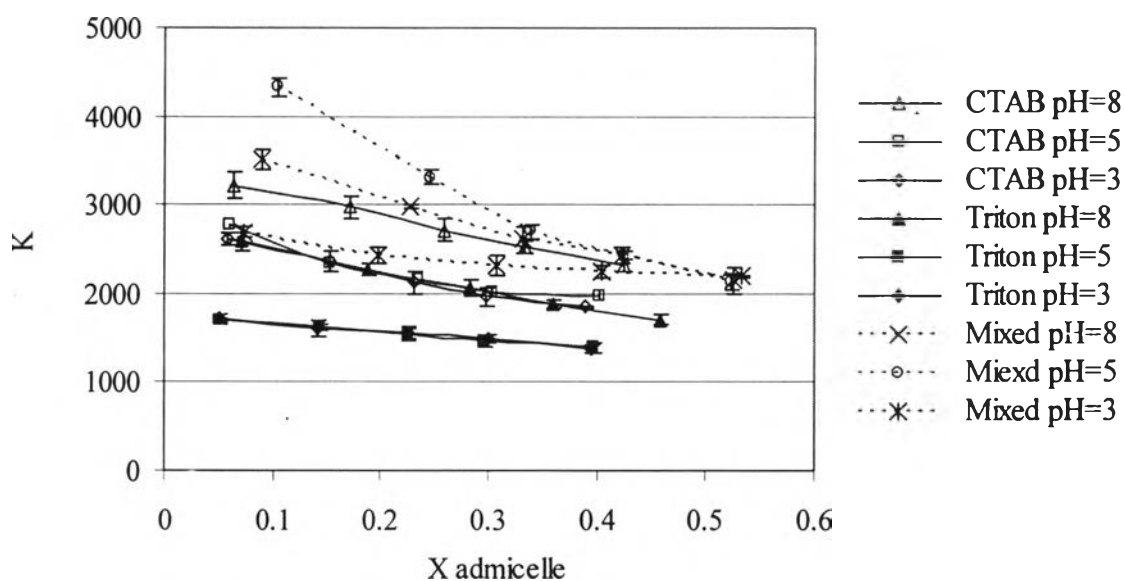


Figure 4.7 Partition coefficient (K) of benzene adsolubilization in various surfactant systems at pH 3, 5, and 8.

4.2.2 Adsolubilization of Toluene

The adsolubilization of toluene was investigated by using a similar approach as for the adsolubilization of benzene. The amount of toluene in the supernatant was measured by headspace GC.

Figure 4.8 shows the adsolubilization isotherms of toluene as a function of the equilibrium concentration of toluene in the aqueous phase at pH 3, 5, and 8. As expected, the toluene adsolubilization increases with increasing equilibrium concentration of toluene. Comparison of the adsolubilization of toluene

in different surfactant systems shows that the adsolubilization of toluene in the CTAB-alone system is much higher than that in Triton and the mixed systems. The adsolubilized amount appears to be related to the amount of adsorbed surfactant on silica and the packing of surfactant molecules. This can be explained that the CTAB molecules packing tighter than Triton and mixed CTAB/Triton molecules, which is demonstrated by the highest plateau adsorption (Figures 4.1, 4.2, and 4.3). Therefore, it can decrease water penetration into the aggregates and make the core proportionally larger, which would result in a higher adsolubilization for slightly polar compound. For the single surfactant systems the results of the toluene adsolubilization are similar to those observed in the benzene adsolubilization. That is, the amount of adsolubilized toluene at pH 8 is slightly higher than that at pH 5 and pH 3, respectively. The results suggested that increasing surface charge as pH increases leads to a higher polarity to the admicelle, thus a higher affinity for toluene which is polarizable.

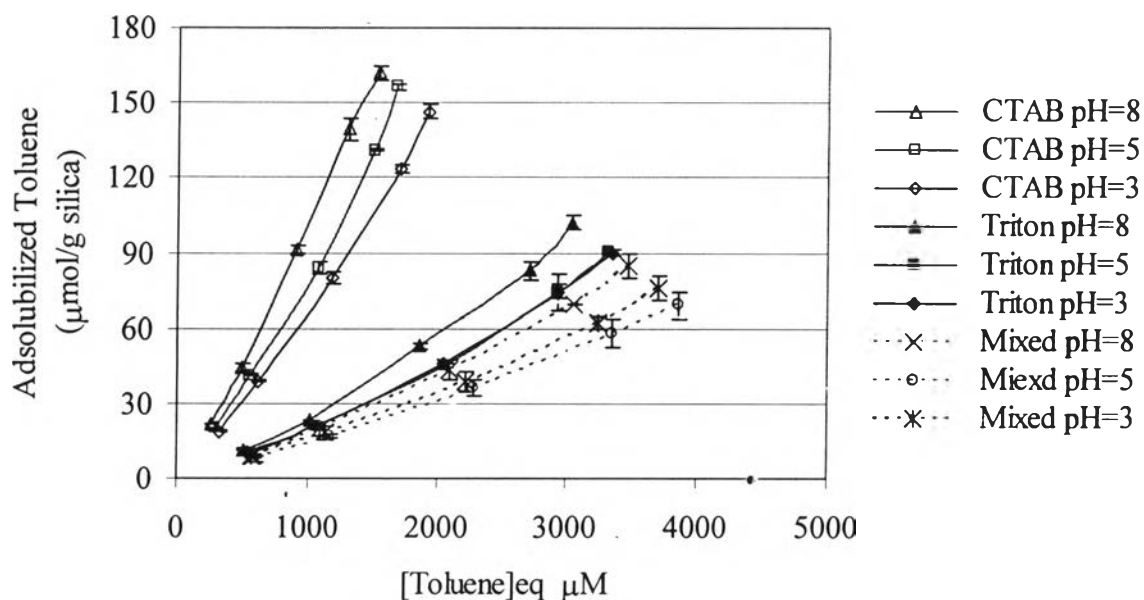


Figure 4.8 Adsolubilization of toluene in various surfactant systems at pH 3, 5, and 8.

In mixed surfactant system, it is obvious that the presence of Triton in the system results in lowered toluene adsolubilization as explained earlier in benzene adsolubilization. However, when comparing mixed CTAB/Triton to pure Triton

system, one can see that the adsolubilization of toluene in mixed system is lower than that in Triton system despite little difference in the amount of adsorbed surfactant on silica (Appendix A-1). This indicates that the adsolubilization of toluene does not depend only on the amount of surfactant adsorbed on silica. One possible explanation for the toluene adsolubilization behavior in the mixed system is that the reduced repulsion between head groups of CTAB and Triton leads to tighter packing of the admicelles, thus making it more difficult for the branched-structure toluene to penetrate into the admicelle than for benzene.

Figure 4.9 is the plot of the partition coefficient (K) versus the mole fraction of toluene in admicelle ($X_{\text{admicelle}}$) at all pH values. It can be seen that all systems show the partition coefficients remain relatively constant as mole fraction of toluene in admicelle increases. Since toluene is a slightly polar organic solute, toluene tends to partition into both the core and palisade layers of the admicelle as seen in previous study (Pradubmook *et al*, 2003).

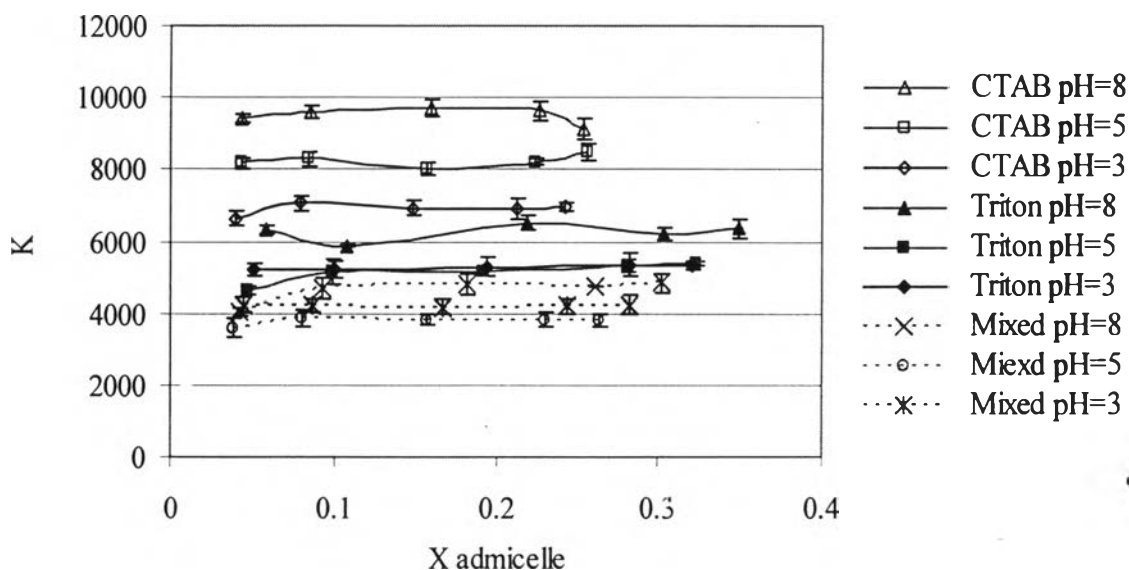


Figure 4.9 Partition coefficient (K) of toluene adsolubilization in various surfactant systems at pH 3, 5, and 8.

4.2.3 Adsolubilization of Ethylbenzene

The adsolubilization behavior of surfactants adsorbed on silica surface for ethylbenzene was investigated by using a similar approach as for the

adsolubilization of benzene and toluene. Figure 4.10 compares the adsolubilization of ethylbenzene in CTAB, Triton, and mixed CTAB/Triton admicelles at the studied pH values. Again, as expected, the amount of adsolubilized ethylbenzene increases with increasing bulk ethylbenzene concentration. It can also be seen that the ethylbenzene adsolubilization in the pure CTAB system is much higher than those in Triton and mixed CTAB/Triton systems. This appears to relate to the amount of surfactant adsorbed on silica as seen in Figures 4.1, 4.2, and 4.3. In addition, this also may be due to the tighter packing of CTAB molecules from the highest CTAB adsorption and the increase in the surface charge as pH increases which lead to reduce the penetration of water molecules into the palisade region of the admicelle and, consequently, increasing the relative size of the core region. Since ethylbenzene, which is non-polar solute, is capable of adsolubilization into the core region, this increase results in a more favorable adsolubilization.

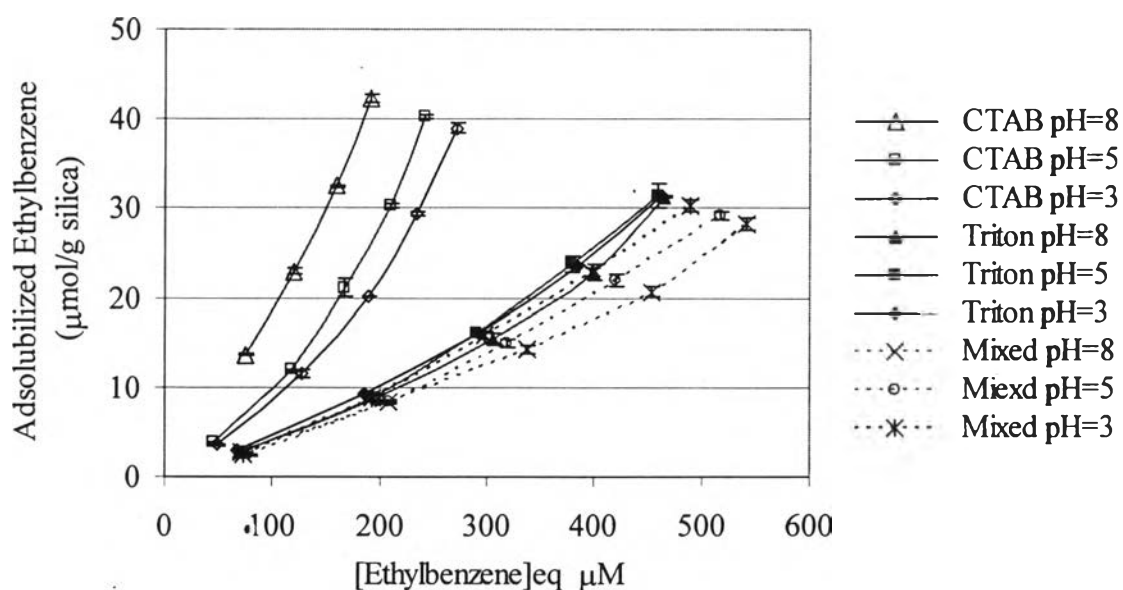


Figure 4.10 Adsolubilization of ethylbenzene in various surfactant systems at pH 3, 5, and 8.

In pure Triton system, it can be seen for all pH values that the adsolubilization of ethylbenzene are quite similar. This can be explained that, although the increase in pH leads to a higher polarity of the admicelle, but ethylbenzene is quite non-polar, and thus pH does not affect the ethylbenzene

adsolubilization in the pure Triton system. When comparing the single- and mixed-surfactant systems, the results show that the ethylbenzene adsolubilizations are similar to those observed in the toluene adsolubilization in which the structural effect of the solute is clearly observed. Ethylbenzene has branched structure and thus, it can not easily penetrate into the admicelle. Consequently, the adsolubilization of ethylbenzene in mixed CTAB/Triton system is lower than that observed in the pure systems due to tighter packing of the mixed admicelles as explained earlier.

Figure 4.11 shows the plot of the partition coefficient (K) versus the mole fraction of ethylbenzene in the admicelle at all pH values. The trend observed from the plot shows a very similar behavior in all systems studied with the partition coefficient of ethylbenzene increasing with increasing mole fraction in the admicelle. In contrast to benzene, ethylbenzene should adsolubilize into the core layer of the admicelle since ethylbenzene is quite non-polar and has a low aqueous solubility.

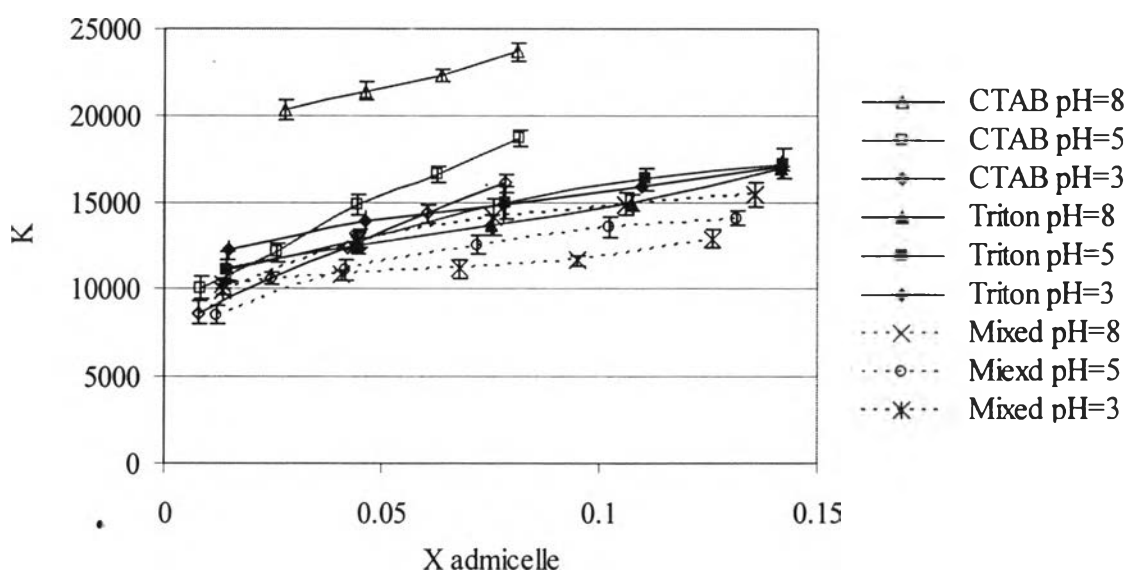


Figure 4.11 Partition coefficient (K) of ethylbenzene adsolubilization in various surfactant systems at pH 3, 5, and 8.