CHAPTER IV
RESULTS AND DISCUSSION

4.1 Surfactant Adsorption

In this part of the study, the adsorption of single surfactant and mixed anionic/nonionic surfactants at various molar ratios, and at pH 3.5 on aluminum oxide were studied.

4.1.1 Single-Surfactant Systems

4.1.1.1 Sodium Dodecyl Sulfate (SDS)

Figure 4.1 shows the adsorption isotherm of SDS at pH 3.5 on the aluminum oxide plotted on a log-log scale. This isotherm represents the characteristic regions II, III, and IV. The critical micelle concentration (CMC) of SDS adsorbed on the aluminum oxide could be determined from the adsorption isotherm which was found to be approximately 9000 μM, which agrees well with the reported value (Rosen, 1989). From the plateau region, it can be seen that the maximum SDS adsorption on the aluminum oxide was approximately 680 μmole/g alumina, which is greater than the maximum SDS adsorption on the aluminum oxide at high pH (Adak *et al.*, 2005; Gawade *et al.*, 2005). This is due to the fact that the surface of the aluminum oxide becomes more positively charge at pH which is lower than the point of zero charge (PZC) of the aluminum oxide, that is, a pH of 8.5.

4.1.1.2 Polyoxyethylene Octyl Phenyl Ether (Triton X-100)

Figure 4.2 shows the adsorption isotherm of Triton X-100 at pH 3.5 on the aluminum oxide plotted on a log-log scale. This isotherm shows the characteristic 'S' shape. The critical micelle concentration (CMC) of Triton X-100 adsorbed on the aluminum oxide determined from the adsorption isotherm was found to be approximately 300 μM. This CMC agrees well with the literature value reported by Huang and Gu, 1987. The maximum Triton X-100 adsorption on the aluminum oxide was approximately 0.9 μmole/g alumina.
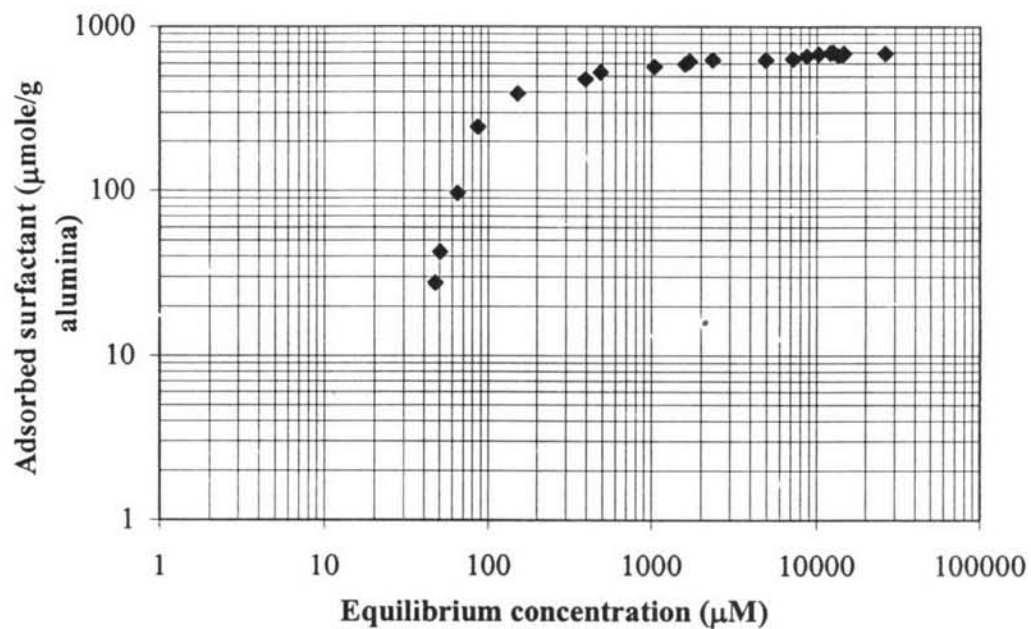
Figure 4.1 Adsorption isotherm of SDS on the aluminum oxide at pH 3.5 and at 30°C.
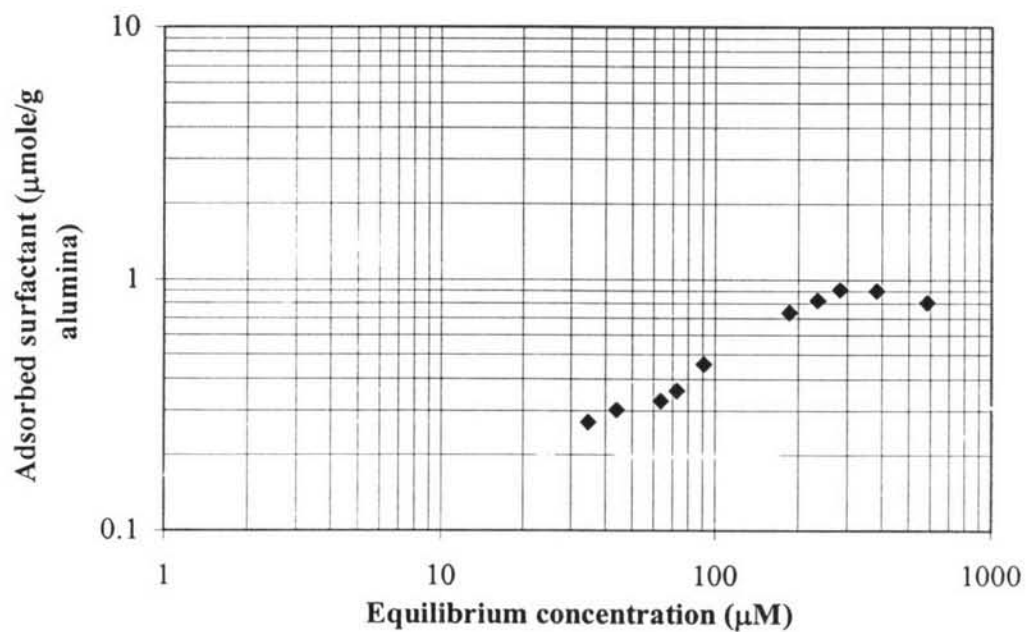

Figure 4.2 Adsorption isotherm of Triton X-100 on the aluminum oxide at pH 3.5 and at 30°C.

From these two figures, a comparison between the adsorption of SDS and Triton X-100 can be made. It is obvious that SDS adsorbs preferably on the aluminum oxide as indicated by a much higher adsorbed surfactant amount. This is attributed to a strong interaction between the anionic surfactant and the aluminum oxide surface which is electrostatically driven. At low SDS concentration, the SDS adsorbs on the aluminum oxide surface by an electrostatic attractive forces between its negatively charged groups and the positively charged aluminum oxide surface, orienting its hydrocarbon chain towards the water phase. As the SDS concentration increases further, the surfactant adsorbs through hydrocarbon chain-chain interaction with neighboring SDS.

In contrast, it is clear from the Triton X-100 adsorption isotherm that the interaction of Triton X-100 with the positively charged aluminum oxide surface is very weak, and does not lead to hemimicelle or admicelle formation (Wang and Kwak, 1999).

4.1.2 Mixed-Surfactant Systems

In this part of the study, the adsorption isotherms of mixed surfactants of SDS and Triton X-100 were studied at the aluminum oxide-water interface using various molar ratios of each surfactant in the mixed surfactant systems. For the mixed SDS/Triton X-100 systems, TOC and UV-VIS spectrophotometer were systematically used to analyze the total surfactant and Triton X-100 concentrations. Then SDS concentration was calculated by subtracting Triton X-100 concentration from the total surfactant concentration. The results can thus be presented in terms of the total surfactant concentrations (combined SDS and Triton X-100 concentrations) and the individual surfactant concentration.

4.1.2.1 Total Surfactant Adsorption

Figure 4.3 shows the total surfactant adsorption isotherms of the mixed surfactant systems at various molar ratios of SDS/Triton X-100, plotted on a log-log scale. The shape is intermediate between that of the ionic and the nonionic surfactant alone, showing some linear regions but not particularly showing sharp boundaries or inflection points between regions. Even though the adsorption density of Triton X-100 is considerably larger than the density without adsorbed SDS, the

adsorption of Triton X-100 in the presence of adsorbed SDS is still smaller than the pure SDS adsorption density.

It is also observed from the experiments that the amount of adsorbed surfactant onto the aluminum oxide increases with decreasing Triton X-100 molar ratio in the mixed surfactant systems. The order of increasing of amount of adsorbed surfactant in molar ratios of SDS/Triton X-100 is 1:3, 1:1 and 3:1, respectively. It is suggested that the addition of Triton X-100 reduces the electrostatic repulsion between SDS headgroup in the mixed surfactant systems. However, the decrease in the adsorption of SDS upon addition of Triton X-100 is attributed to the competition between the bulky nonionic Triton X-100 and SDS (Esumi *et al.*, 2000).
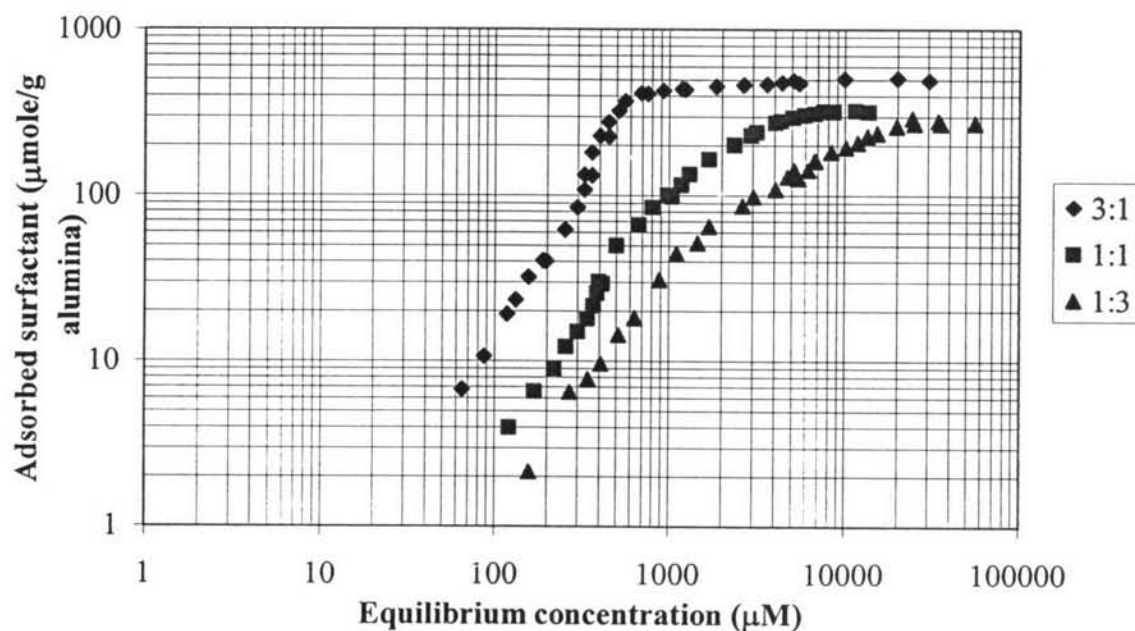

Figure 4.3 Adsorption isotherms of total surfactant in mixed SDS/Triton X-100 adsorption on the aluminum oxide at various SDS/Triton X-100 molar ratios at pH 3.5 and at 30°C.

4.1.2.2 Sodium Dodecyl Sulfate (SDS) Adsorption

Figure 4.4 shows the adsorption isotherms of SDS on the aluminum oxide in both single- and mixed-surfactant systems at various molar ratios of SDS to Triton X-100, plotted on a log-log scale. All isotherms illustrate the characteristic regions II, III and IV.
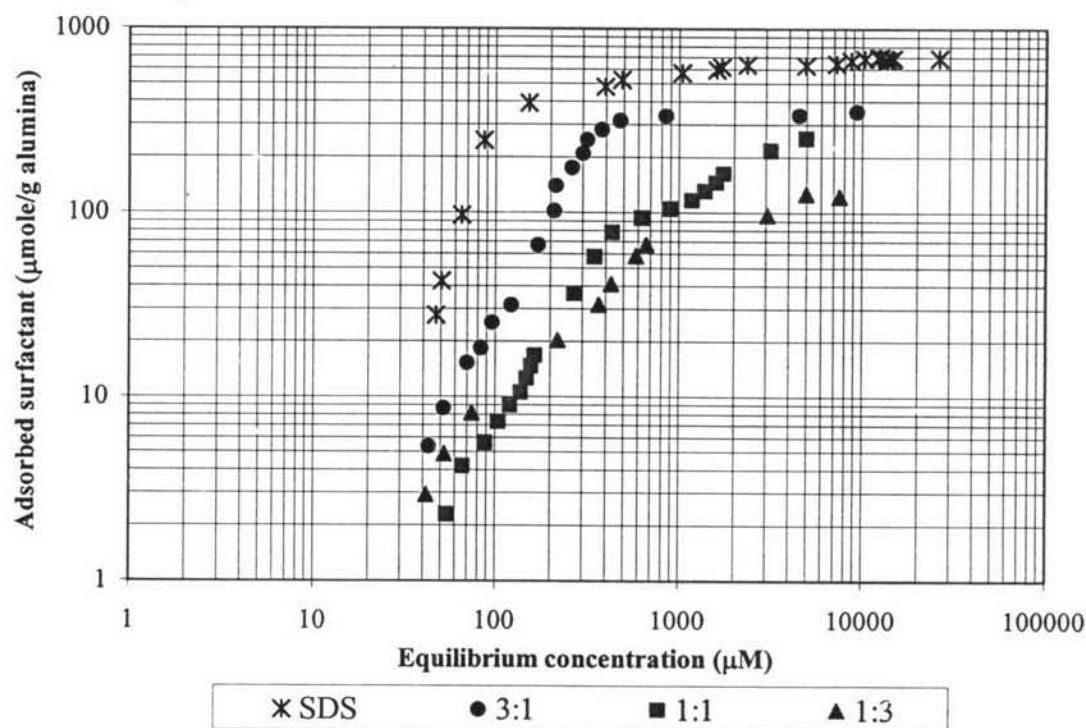

Figure 4.4 Adsorption isotherms of SDS on the aluminum oxide in both single surfactant system and mixed SDS/Triton X-100 systems at various molar ratios at pH 3.5 and at 30°C.

The adsorption of SDS in mixed surfactant systems is slightly decreased by the addition of Triton X-100 at all molar ratios. The decrease in the adsorption isotherms of SDS is probably due to the large volume taken up in the admicelle by Triton X-100 molecules which do not allow tight packing of SDS.

4.1.2.3 Triton X-100 Adsorption

Figure 4.5 shows the adsorption isotherms of Triton X-100 on the aluminum oxide in both single- and mixed-surfactant systems at various molar ratios of SDS/Triton X-100, plotted on a log-log scale. From this figure, it is observed that the adsorption of Triton X-100 increases markedly in the presence of adsorbed SDS. In addition, the slope of Triton X-100 isotherm in region II also increases with increasing SDS content. It is expected that increased co-adsorption of Triton X-100 eventually leads to almost all SDS monomers being extracted onto the surface because it dues to decreased electrostatic repulsion between headgroups of SDS (Wang and Kwak, 1999).
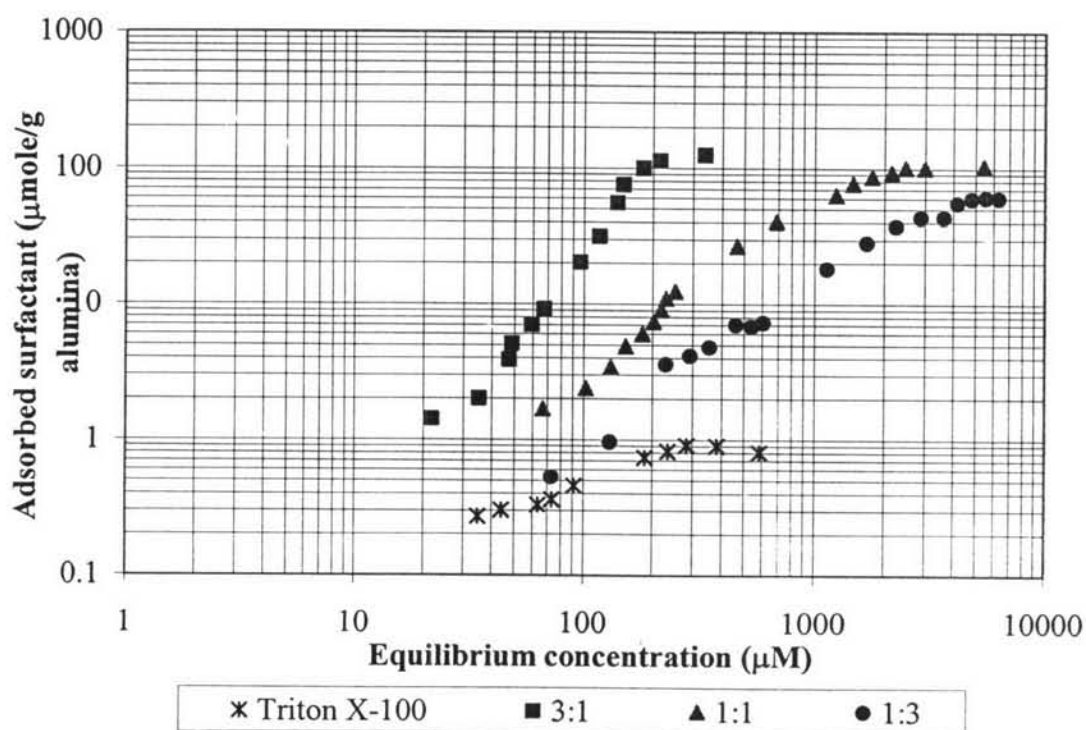

Figure 4.5 Adsorption isotherms of Triton X-100 on the aluminum oxide in both single surfactant system and mixed SDS/Triton X-100 systems at various molar ratios at pH 3.5 and at 30°C.

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-surfactant systems of SDS and Triton X-100 adsorbed on the aluminum oxide surface at three molar ratios of anionic/nonionic surfactants (1:3, 1:1 and 3:1) and at pH 3.5 were investigated. The adsorption isotherm data was used to determine a surfactant feed concentration that would equilibrate below the CMC of the surfactant system being studied. An organic solute was added to equilibrium surfactant/aluminum oxide samples by syringe injections of various amounts into the crimp-sealed vials, up to the water solubility of the solutes. The reported 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 in both the single- and mixed-surfactant systems at pH 3.5. 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 pure system of SDS, whereas the lowest is observed in the pure system of Triton X-100. The results suggest that the adsolubilization of benzene may be related to the amount of adsorbed surfactant as the amount of adsorbed SDS is higher than that of Triton X-100 (Figures 4.1 and 4.2).
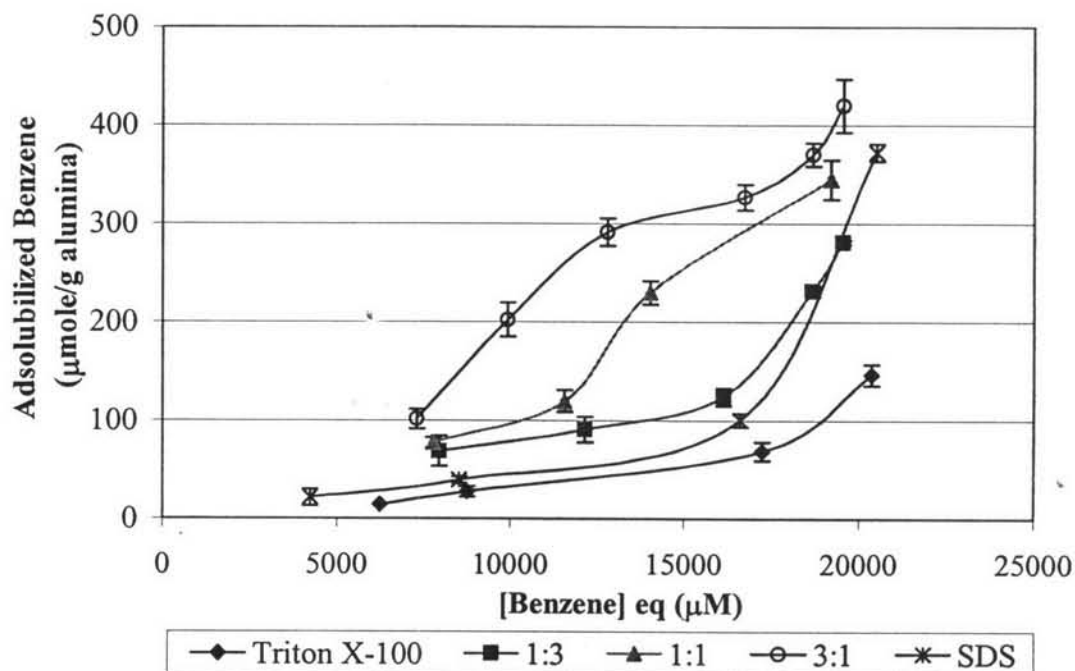
Figure 4.6 Adsolubilization of benzene in both single- and mixed-surfactants systems (SDS/Triton X-100 molar ratios) at pH 3.5 and at 30°C.

In the mixed surfactant systems, the adsolubilization of benzene also may be related to the amount of adsorbed surfactant, which the amount of adsorbed mixed surfactant of anionic/nonionic ratio at 3:1 is the highest (437 μmole/g alumina) whereas at the ratio 1:3 is the lowest (255 μmole/g alumina) (Figure 4.3).

Comparison between single- and mixed-surfactant systems reveals that the pure SDS is quite anomalous because there is no clear correlation between the amounts of adsorbed surfactant on the aluminum oxide surface where the pure SDS should theoretically have a higher amount of adsolubilized benzene than the mixed-surfactant systems. As benzene is a polar organic solute with no attached branch, thus, it should primarily adsolubilize in the palisade region and may possibly adsolubilize in the core region. For the pure SDS system, the admicelles pack in a looser fashion, improving the ability of water molecules to penetrate into the admicelles and consequently increasing the relative size of the palisade region. In contrast, in the mixed-surfactant systems, the tighter packing could lead to increasing the hydrophobicity of the admicelles. It is thought that although the relative size of

the palisade region of pure SDS increases, the effect is probably less than the increase of the hydrophobicity of mixed surfactant systems because of the morphology of the admicelle.

Figure 4.7 shows the value of the partition coefficient (K) versus the mole fraction of benzene in the admicelle ($X_{admicelle}$) of pure Triton X-100 system at pH 3.5. It found that K decreases with increasing $X_{admicelle}$. This is probably due to the amount of adsorbed Triton X-100 being the least (0.9 µmole/g alúmina) (Figure 4.2). That means the volume of admicelle is so small that benzene can not adsolubilize to any appreciable amount.
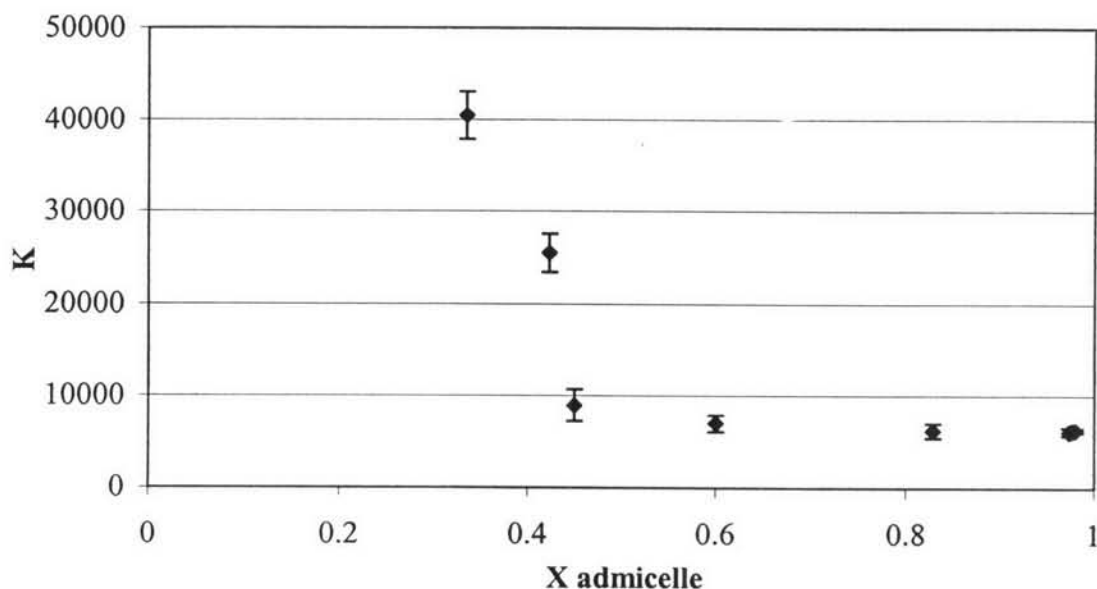

Figure 4.7 Partition coefficient (K) of benzene adsolubilization in pure Triton X-100 system at pH 3.5 and at 30°C.

Figure 4.8 shows the value of the partition coefficient (K) versus the mole fraction of benzene in the admicelle ($X_{admicelle}$) of pure SDS system at pH 3.5. From this curve, it can be seen that the partition coefficient of benzene increasing as the mole fraction of the benzene in the admicelle increases. This suggests that the benzene partitions primarily into the palisade regions in the admicelle.
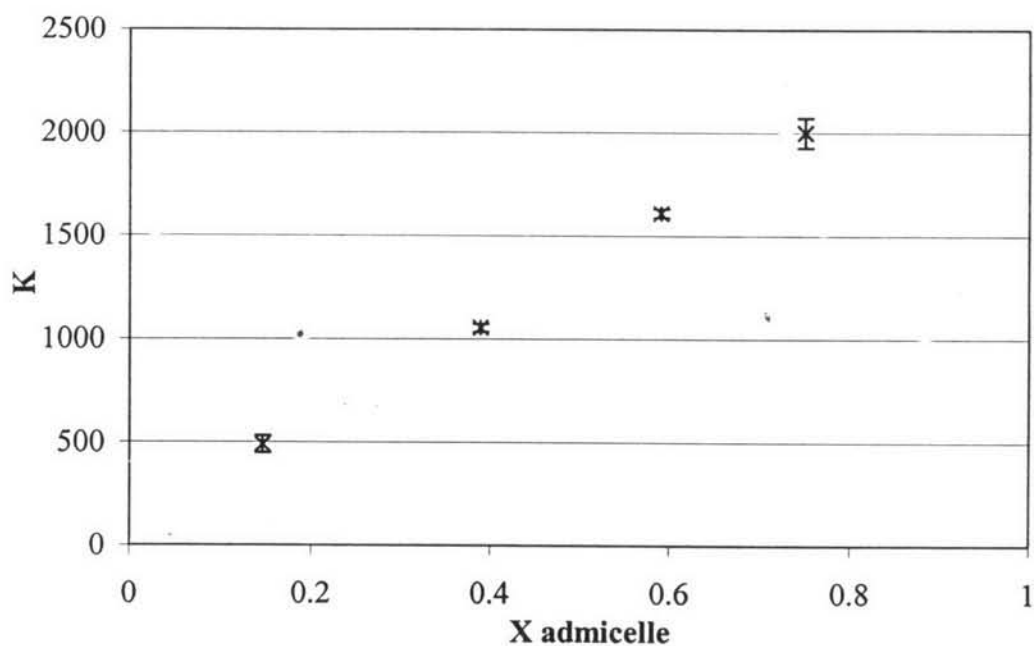
Figure 4.8 Partition coefficient (K) of benzene adsolubilization in pure SDS system at pH 3.5 and at 30°C.

Figure 4.9 shows the value of the partition coefficient (K) versus the mole fraction of benzene in the admicelle ($X_{admicelle}$) for mixed surfactant systems at pH 3.5. The general trends observed in each plot are similar with the partition coefficient of benzene in pure SDS system (Figure 4.8). Thus, the morphology of adsolubilized benzene in the admicelles of mixed surfactant systems is the same as that of the pure SDS system. The presence of Triton X-100 enhances the adsolubilization of benzene at lower mole fractions in the admicelle, which may be due to the looser admicelle structure.
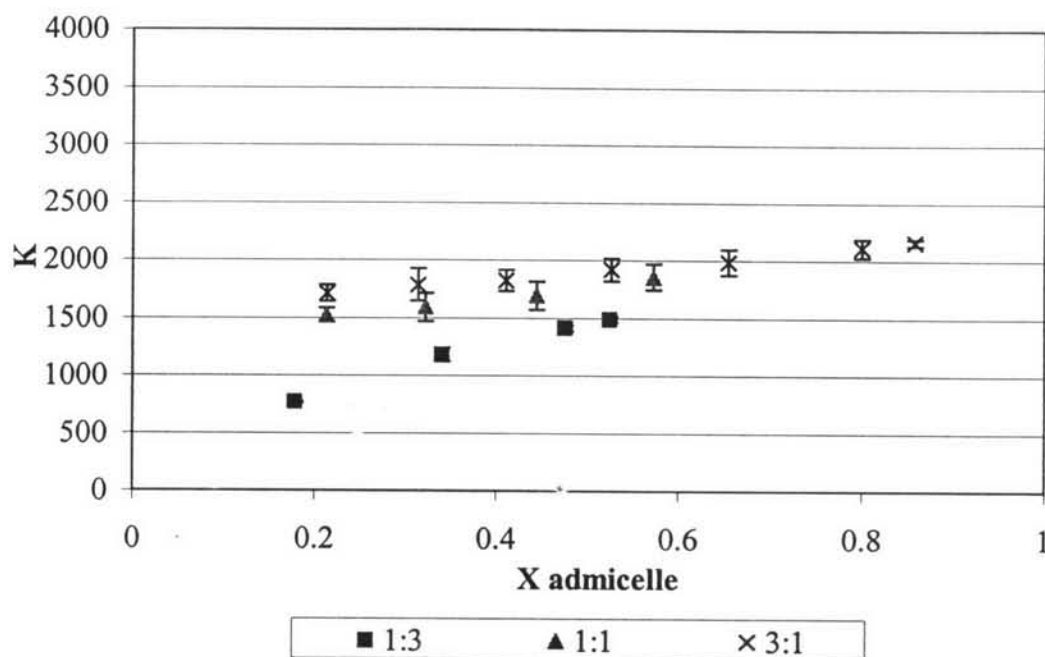
Figure 4.9 Partition coefficient (K) of benzene adsolubilization in mixed surfactant systems (SDS/Triton X-100 molar ratios) at pH 3.5 and at 30°C.

4.2.2 Adsolubilization of Toluene

Figure 4.10 shows the adsolubilization isotherms of toluene as a function of the equilibrium concentration of toluene in the aqueous phase at pH 3.5 in both single- and mixed-surfactant systems. The results show that the curve of Triton X-100 is the least and quite constant around 20 μmole/g alumina but the other curves (ie. SDS) increase with increasing equilibrium concentration of toluene. It is found that, for both single- and mixed-surfactant systems, the adsolubilization of toluene is similar to the adsolubilization of benzene. That is, the adsolubilization of toluene appears to be related to the amount of adsorbed surfactant (Figures 4.1, 4.2 and 4.3).
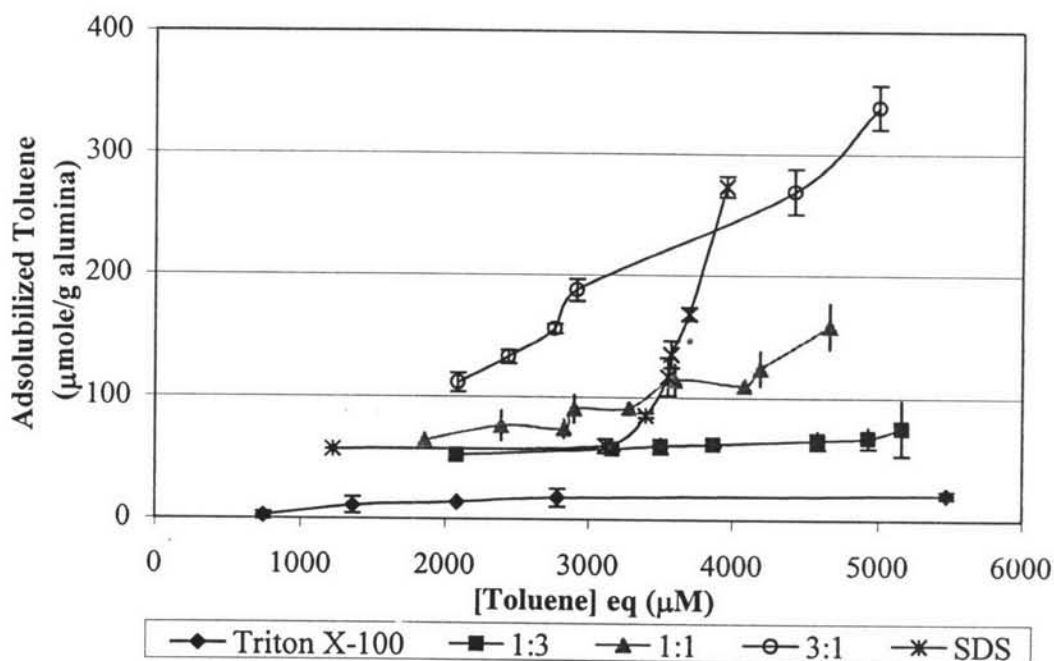
Figure 4.10 Adsolubilization of toluene in both single- and mixed-surfactants systems (SDS/Triton X-100 molar ratios) at pH 3.5 and at 30°C.

In the mixed surfactant systems, the adsolubilization of toluene also may be related to the amount of adsorbed surfactant (Figure 4.3). From this graph, it can be seen that in the molar ratio of mixed surfactant at 3:1 has the adsolubilization behavior similar with the pure SDS system where the high concentration.

Toluene, having intermediate polarity, is expected to adsolubilize into both the palisade and core regions of the admicelle. In the first half of each curve, it looks like the behavior of the adsolubilization of benzene as explained above. But in the second half of each curve, SDS is sharply increased, higher than the mixed-surfactant systems. This may be due to the "looser packing" of SDS where toluene can adsolubilize. Because the structure of toluene has the methyl group as branch, it is difficult to adsolubilize. Thus, the mixed-surfactant systems, which are tightly packed, can adsolubilize toluene less than the pure SDS system.

Figure 4.11 shows the value of the partition coefficient (K) versus the mole fraction of toluene in the admicelle ($X_{admicelle}$) of pure Triton X-100 system at pH 3.5. It found that the curve of K value decreases with increasing $X_{admicelle}$. This

due to the amount of adsorbed surfactant is the least (0.9 μmole/g alumina) (Figure 4.2) so toluene can not more adsolubilize in this admicelles.
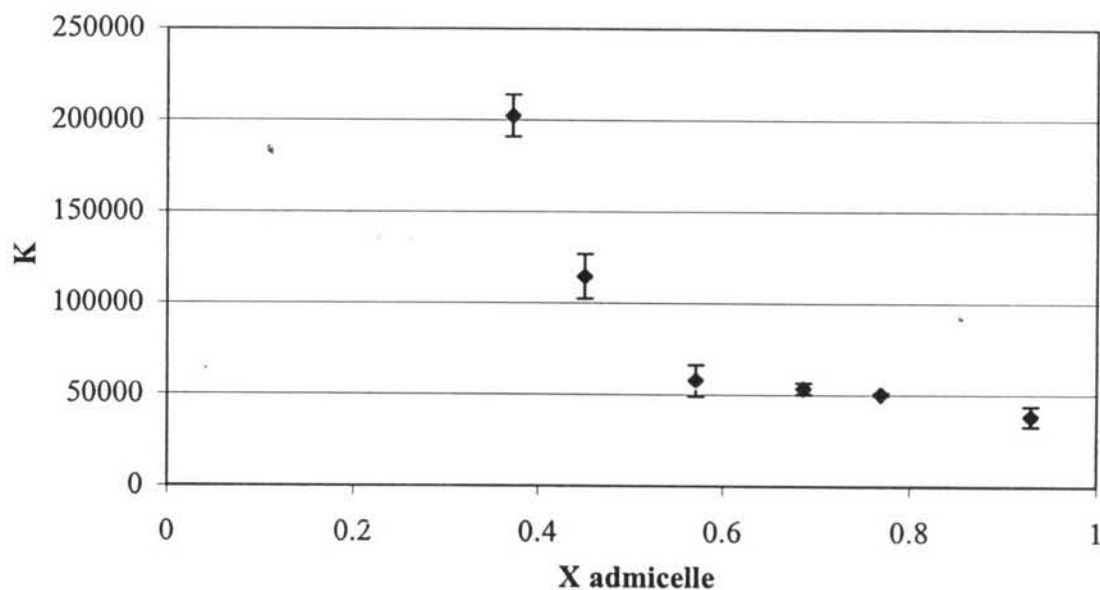

Figure 4.11 Partition coefficient (K) of toluene adsolubilization in pure Triton X-100 system at pH 3.5 and at 30°C.

Figure 4.12 shows the value of the partition coefficient (K) versus the mole fraction of toluene in the admicelle ($X_{admicelle}$) of pure SDS system at pH 3.5. From this curve, it can be seen that the partition coefficient of toluene increasing as the mole fraction of the toluene in the admicelle increases. This suggests that the toluene partitions primarily into the palisade regions then into the core regions of the admicelle. From the looser packing of SDS molecules in the admicelles, thus, toluene can more adsolubilized in this admicelles.
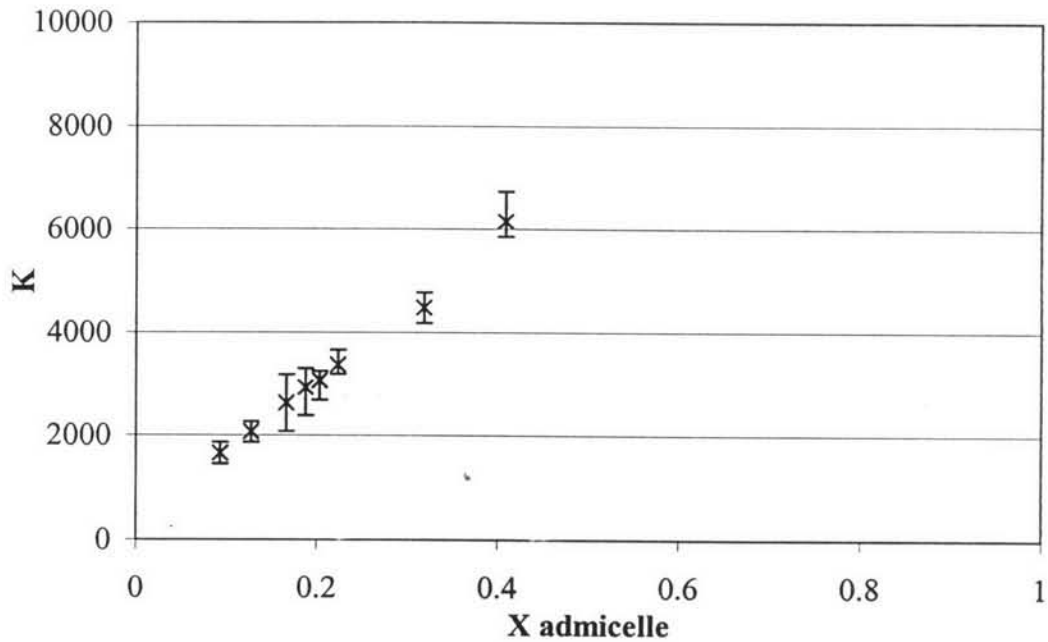
Figure 4.12 Partition coefficient (K) of toluene adsolubilization in pure SDS system at pH 3.5 and at 30°C.

Figure 4.13 shows the value of the partition coefficient (K) versus the mole fraction of toluene in the admicelle ($X_{admicelle}$) at mixed surfactant systems and at pH 3.5. It can be seen that the partition coefficients remain relatively constant as mole fraction of toluene in the admicelle increases. Since the toluene is a slightly polar organic solute and has methyl group as branch, it can partition into both the palisade and core layers of the admicelle and, afterwards, it is difficult to adsolubilize in the admicelle because of its branch.
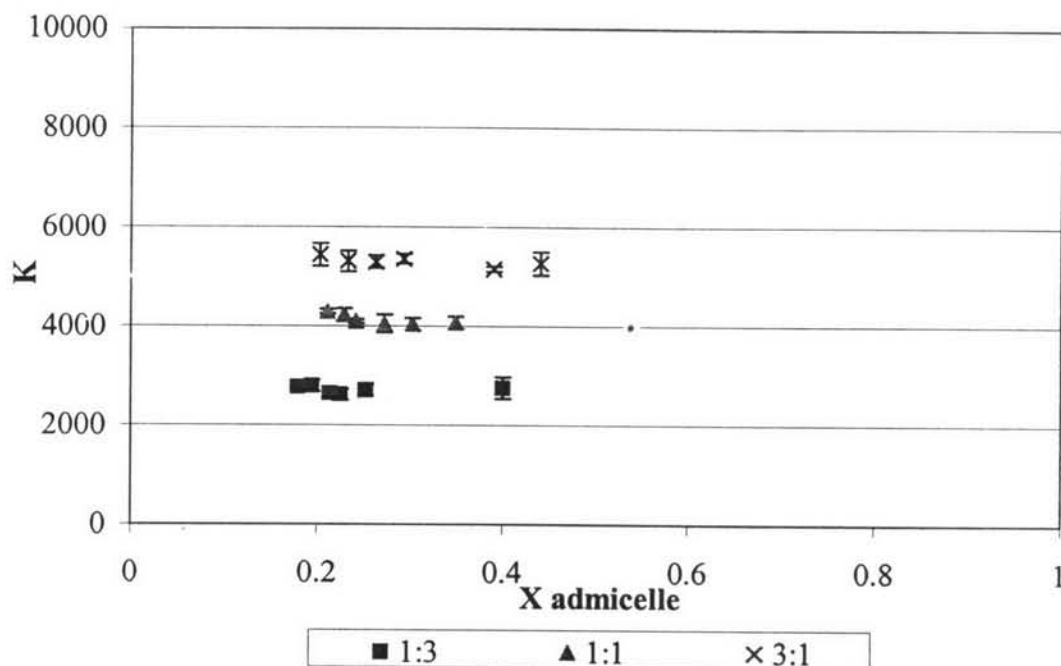
Figure 4.13 Partition coefficient (K) of toluene adsolubilization in mixed surfactant systems (SDS/Triton X-100 molar ratios) at pH 3.5 and at 30°C.

4.2.3 Adsolubilization of Ethylbenzene

Figure 4.14 shows the adsolubilization isotherms of ethylbenzene in both the single- and mixed-surfactant systems at pH 3.5. The adsolubilization of ethylbenzene increases with increasing equilibrium concentration of ethylbenzene for all systems. From the results, it is found that the adsolubilization of ethylbenzene in single surfactant systems may also be related to the amount of adsorbed surfactant which the amount of adsorbed SDS is higher than that of Triton X-100 (Figures 4.1 and 4.2).
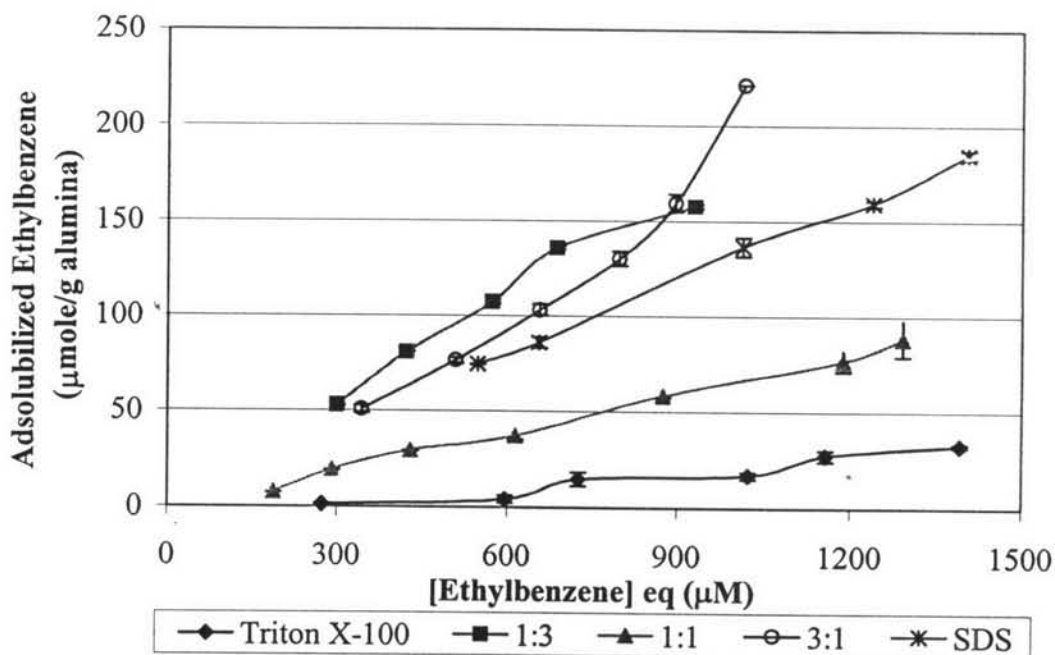
Figure 4.14 Adsolubilization of ethylbenzene in both single- and mixed-surfactants systems (SDS/Triton X-100 molar ratios) at pH 3.5 and at 30°C.

In the mixed surfactant systems, the adsolubilization behavior is the same as in the single surfactant system that the adsolubilization of ethylbenzene increase with increasing the concentration of ethylbenzene in the bulk phase. From figure 4.14, it is found that the molar ratio of 1:3 is the highest amount of adsolubilized ethylbenzene. It may be due to the synergism effect that this ratio presents more Triton X-100 which is a nonionic surfactant and ethylbenzene is a non-polar solute so it corresponds to the "like dissolved like" rule. Therefore, in this ratio only, ethylbenzene can adsolubilize in the palisade region more than the other ratios because most of this palisade region is Triton X-100. However, at the other ratios, 3:1 and 1:1, are still corresponded with the amount of adsorbed surfactant on the aluminum oxide (Figure 4.3). This synergism may be due to increasing polarity with increasing amounts of SDS in the admicelle, thus, the adsolubilization of ethylbenzene decreases.

Comparing the single- and mixed-surfactant systems, SDS is more loosely packed. And since ethylbenzene has the ethyl group, it can adsolubilize in

pure SDS more than in the other systems. However, the polarity of SDS does not correspond to the polarity of ethylbenzene, which is a non-polar solute. Thus, the amount of adsolubilized ethylbenzene in pure SDS system is not high enough to adsolubilize.

Figure 4.15 shows the value of the partition coefficient (K) versus the mole fraction of ethylbenzene in the admicelle ($X_{admicelle}$) of pure Triton X-100 system at pH 3.5. It found that the partition coefficient of ethylbenzene decreases with increasing $X_{admicelle}$. This due to the amount of adsorbed surfactant is the least (0.9 μmole/g alumina) (Figure 4.2) so ethylbenzene can not more adsolubilize in this admicelles.
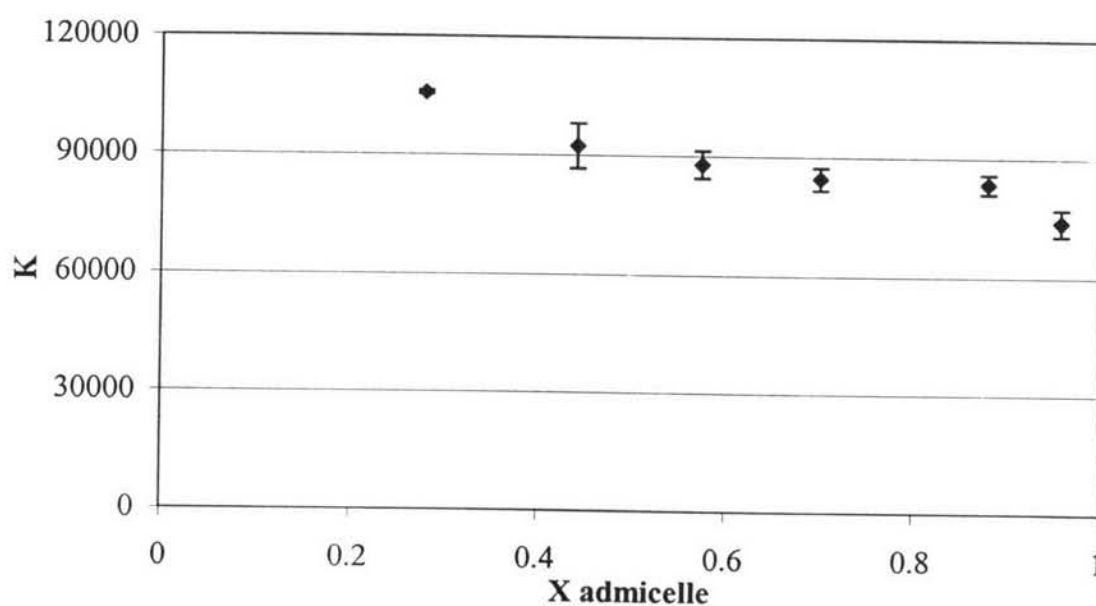

Figure 4.15 Partition coefficient (K) of ethylbenzene adsolubilization in pure Triton X-100 system at pH 3.5 and at 30°C.

Figure 4.16 shows the value of the partition coefficient (K) versus the mole fraction of ethylbenzene in the admicelle ($X_{admicelle}$) of pure SDS system at pH 3.5. It can be seen that the partition coefficient of ethylbenzene decreasing with increasing mole fraction in the admicelle. Since the ethylbenzene is a non-polar organic solute and has ethyl group as branch, it can partition into the core layers of

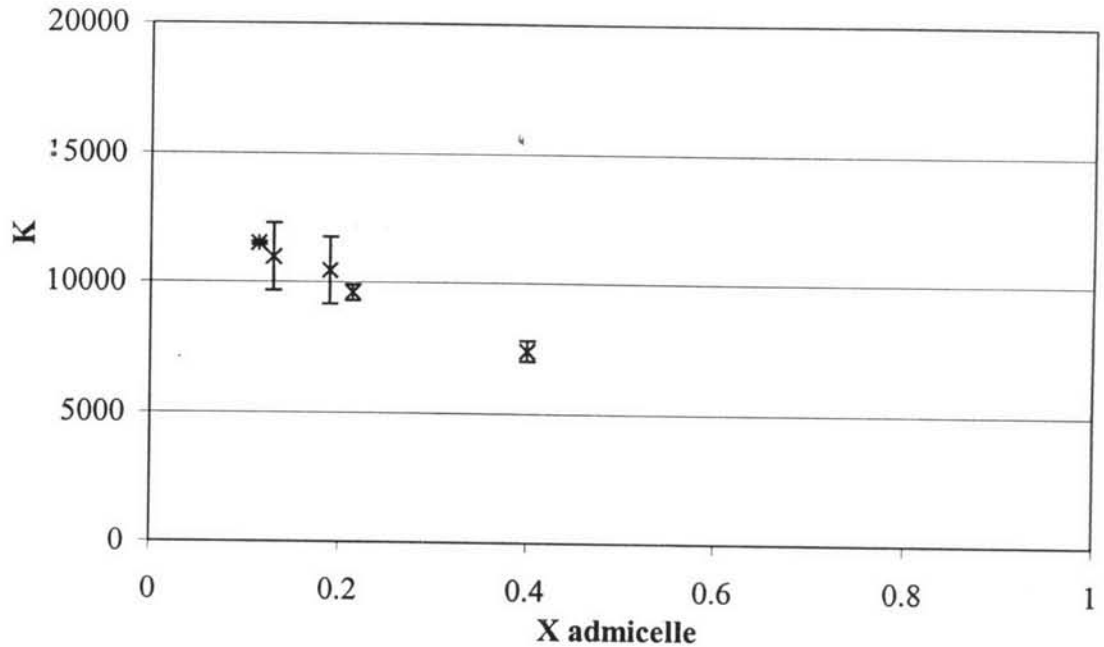the admicelle and, afterwards, it is very difficult to adsolubilize in the admicelle because of its long branch.

Figure 4.16 Partition coefficient (K) of ethylbenzene adsolubilization in pure SDS system at pH 3.5 and at 30°C.

Figure 4.17 shows the value of the partition coefficient (K) versus the mole fraction of ethylbenzene in the admicelle ($X_{admicelle}$) at mixed surfactant systems and at pH 3.5. The trend observed from the plot is similar behavior with the pure SDS system (Figure 4.16). Thus, the morphology of adsolubilization of ethylbenzene in the admicelles of mixed surfactant systems is the same as that of the pure SDS system.
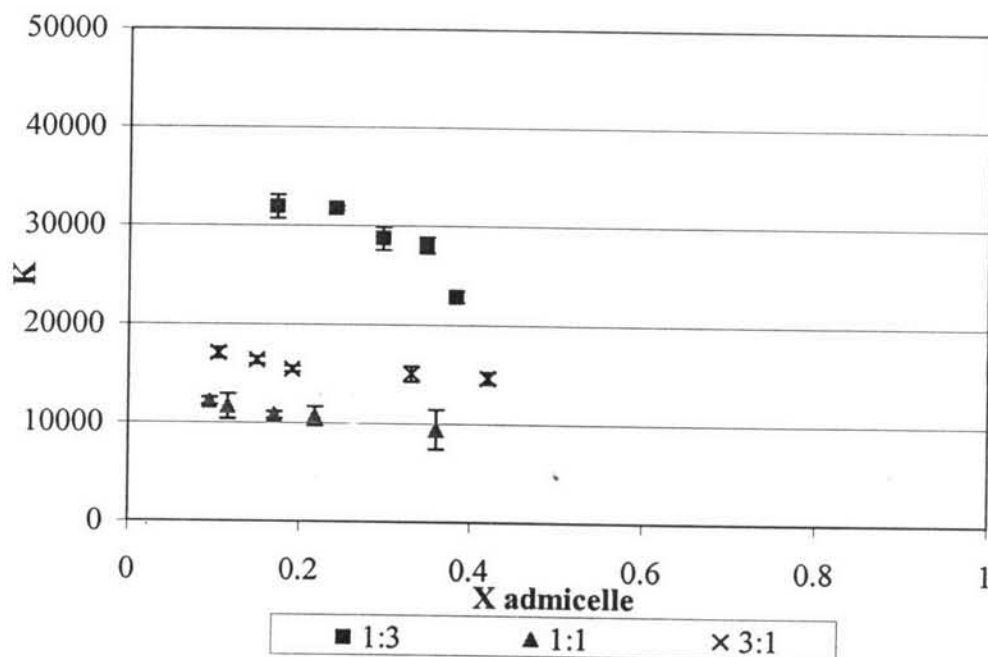
Figure 4.17 Partition coefficient (K) of ethylbenzene adsolubilization in mixed surfactant systems (SDS/Triton X-100 molar ratios) at pH 3.5 and at 30°C.

The effect of type of surfactants in each of the organic solutes can be observed in Figure 4.18 and Figure 4.19.

Figures 4.18 shows the adsolubilization isotherms of the three model organic solutes in pure SDS system at pH 3.5 and at 30°C. It is noticed that among all solutes studied benzene is the highest in the adsolubilized amount, followed by toluene and ethylbenzene. This may be due to the structure of organic solutes as benzene is the smallest structure and has no attached branches, whereas toluene has an attached methyl group and ethylbenzene has an attached ethyl group. Thus solute with long branch would be more difficult to adsolubilize in the admicelle than the short branch one because branching causes a tangled condition, thus hindering the adsolubilization.
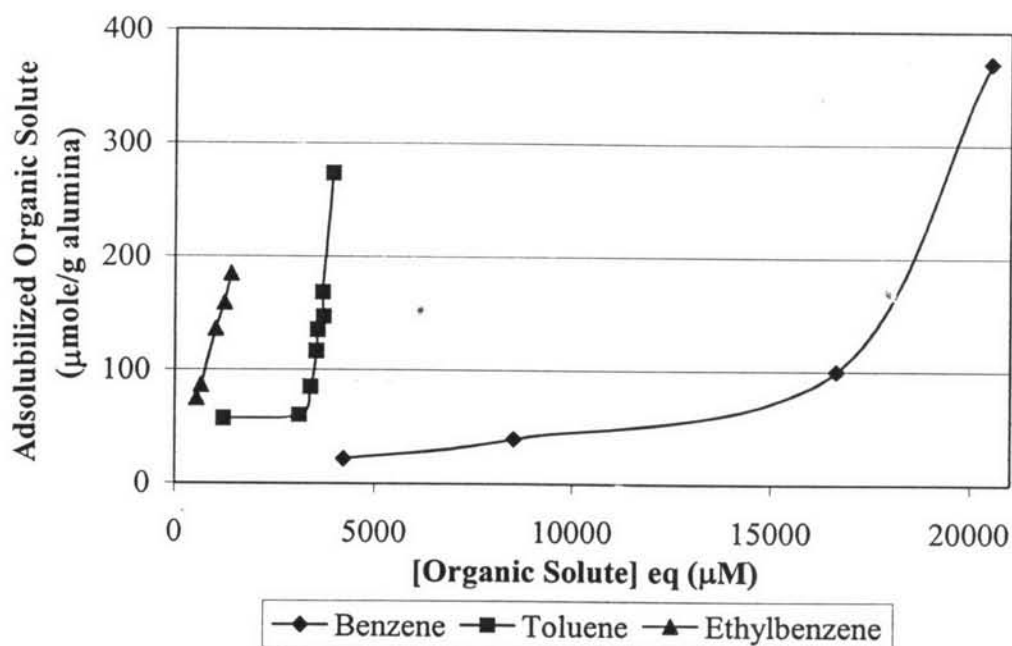
Figure 4.18 The adsolubilization isotherms of organic solutes in pure SDS system at pH 3.5 and at 30°C.

Figures 4.19 shows the adsolubilization isotherms of all three organic solutes in pure Triton X-100 system at pH 3.5 and at 30°C. It is also observed that benzene has the highest adsolubilized amount, followed by ethylbenzene and toluene, respectively. This may be due to the structure and properties of the organic solutes. Benzene has the smallest structure with no attached branch, thus it is easier to adsolubilize in the admicelle than other solutes. The amount of adsolubilized ethylbenzene is more than that of toluene which is probably due to the polarity of the admicelle, formed by Triton X-100. As ethylbenzene is a nonpolar organic solute, whereas toluene is an intermediate polarity organic solute, therefore ethylbenzene should adsolubilize more than toluene, because ethylbenzene can penetrate into both the palisade and core layers of the admicelle; whereas toluene can adsolubilize in only the core layer of Triton X-100 admicelle.
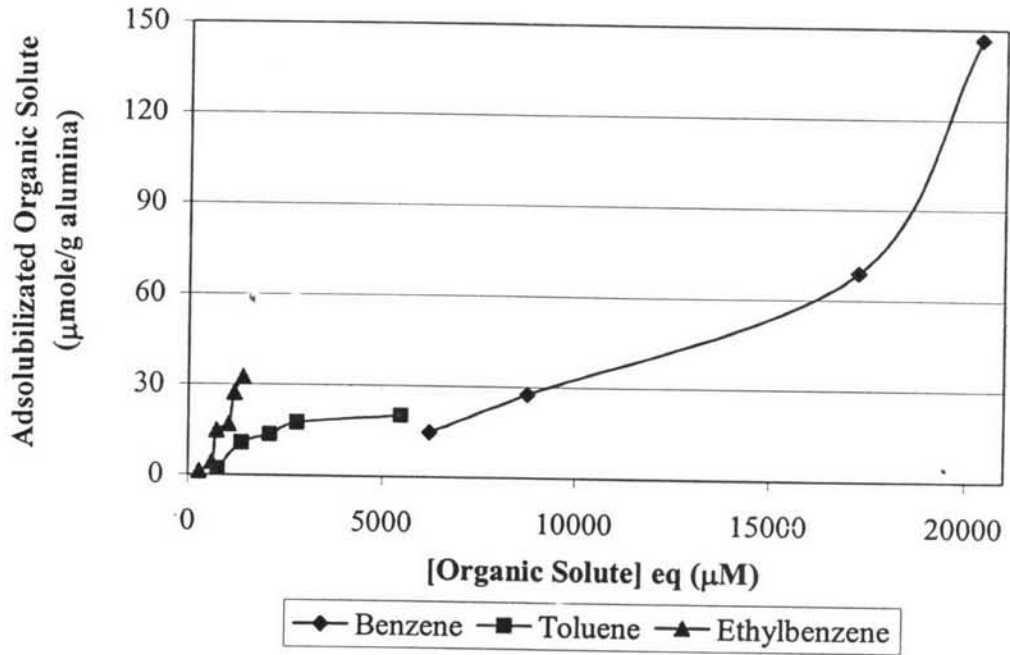
Figure 4.19 The adsolubilization isotherms of organic solutes in pure Triton X-100 system at pH 3.5 and at 30°C.

4.3 Comparison with Previous Work

The effect of pH on adsolubilization of organic compounds in mixed cationic-nonionic surfactant admicelles was studied by Jermjarung (2005). The results showed the adsorption isotherms of a cationic surfactant (CTAB), a nonionic surfactant (Triton X-100), and the mixed molar ratio of 1:1 of CTAB/Triton X-100 adsorbed on precipitated silica and also indicated the adsolubilization isotherms of organic solutes (benzene, toluene and ethylbenzene) in both single- and mixed-surfactant systems.

When comparing to Jermjarung's work, this study used different type of substrate which is the aluminum oxide (positively charge surface) whereas the previous work used the precipitated silica (negatively charge surface). In addition, this work focused on a pH of 3.5 as the PZC of aluminum oxide is 8.5 in order to keep the difference of 5 pH units same as the previous work where pH was fixed at 8

as the PZC of precipitated silica is 3. Thus, the difference in pH values which can be considered as the driving force is the same between the previous study and this work.

Thus, the comparison of the amount of adsorbed surfactant and the amount of adsolubilized organic solute in different surfactant systems under the same condition could be done. It reveals that in the adsorption of a single surfactant, the amount of adsorbed SDS onto aluminum oxide (680 μmol/g alumina) is slightly higher than the amount of adsorbed CTAB onto precipitated silica (620 μmol/g silica). This may be due to the bulkiness of cationic surfactant headgroups, which is bigger than that of anionic surfactant headgroups. For a nonionic surfactant, the amount of adsorbed Triton X-100 onto aluminum oxide (0.9 μmol/g alumina) is much less than the amount adsorbed onto precipitated silica (300 μmol/g silica). This may be due to the fact that the dominant interaction between the nonionic surfactant and the precipitated silica surface is hydrogen bonding (Penfold *et al.*, 2002). In the adsolubilization part, the amount of adsolubilized organic solute appeared to be correspond to the amount of adsorbed surfactant. Thus, the amount of adsolubilized organic solute in the SDS system is greater than that of the CTAB system; whereas the amount of adsolubilized organic solute in Triton X-100 adsorbed on aluminum oxide is less than that of Triton X-100 adsorbed on precipitated silica. In the mixed surfactant system, it was found that the amount of adsorbed SDS/Triton X-100 (325 μmol/g alumina) is less than the amount of adsorbed CTAB/Triton X-100 (450 μmol/g silica). This may be due to the fact that the surface area of precipitated silica (170 m^2/g) is greater than the surface area of aluminum oxide (155 m^2/g). In contrast, the amount of adsolubilized organic solute in the SDS/Triton X-100 system is greater than that in the CTAB/Triton X-100 system. This may be attributed to the synergism of adsolubilization of organic solutes which has a greater effect on the SDS/Triton X-100 than on the CTAB/Triton X-100 system.