CHAPTER IV
RESULTS AND DISCUSSION

4.1 CTAB Adsorption on Hi-Sil 255

In this part of the study, CTAB adsorption has been divided into two sets of experiments in order to study effects of both pH and ionic strength.

4.1.1 Effect of pH

Figure 4.1 shows the CTAB adsorption isotherms at pH 5 and pH 8, plotted on a log-log scale. Both isotherms represent the characteristic regions II, III and IV. For pH = 5, region II occurs at equilibrium concentrations in a range of 40 to 250 µM. For pH 8, region II occurs at equilibrium concentrations in a range of 30 to 180 µM. This figure shows that for every equilibrium concentration, CTAB adsorption on silica at pH 8 is always higher than the adsorption at pH 5. From the plateau region, the maximum CTAB adsorption on silica at pH 5 and pH 8 are approximately 600 and 700 µmol/g silica, respectively. As it is known that the surface of the silica becomes more negatively charged at pH higher than the point of zero charge (PZC) of silica (pH 2-3), increasing the pH leads to higher amount of head on adsorbed surfactant on the precipitated silica.
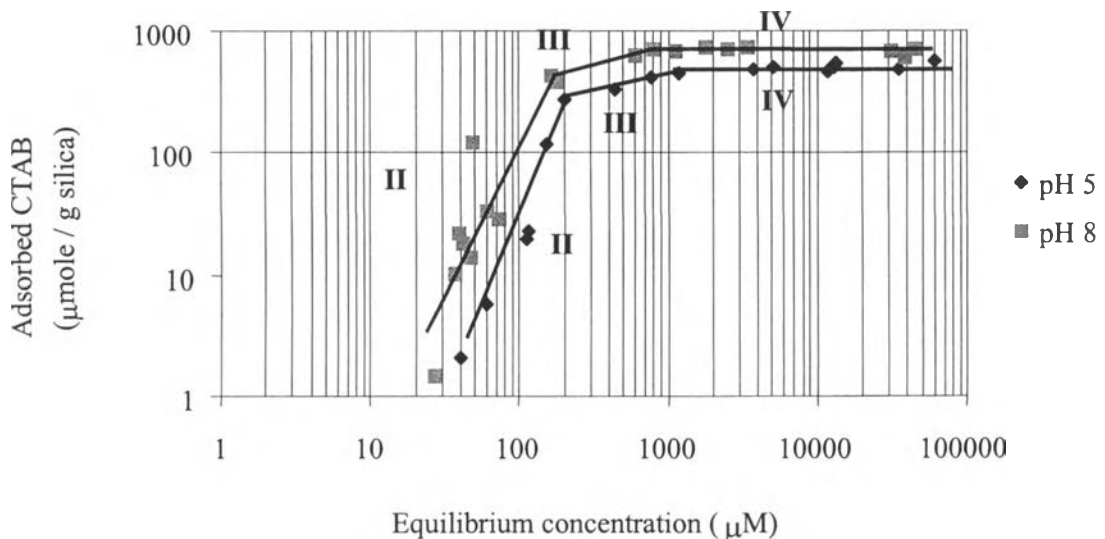

Figure 4.1 Adsorption isotherms of CTAB at pH 5 and pH 8.

From Fig. 4.1, the critical micelle concentration (CMC) of CTAB adsorbed on silica could be determined from the adsorption isotherm. It is found that at pH 8 CMC is approximately 900 μM of equilibrium CTAB concentration in the aqueous phase which agrees well with the published value (Rosen, 1989).

4.1.2 Effect of Ionic Strength

Figure 4.2 shows the CTAB adsorption isotherms at pH 5 and ionic strength (I) of 1, 10 and 100 mM (NaBr), plotted on log-log scale. From the isotherms, it can be seen that the CTAB adsorption at I = 100 mM is higher than those at I = 1 and 10 mM. When compare the isotherms between I = 1mM and I = 10 mM, we can see that CTAB adsorption on silica at I = 10 mM is slightly higher than I = 1 mM, especially at low CTAB concentrations. This can be explained that when the ionic strength of the system is increased, the repulsion between head group of cationic surfactant (CTAB) is reduced by anion (Br⁻). Therefore increasing ionic strength of the system leads to higher amount of head on adsorbed surfactant on the surface and thus higher CTAB adsorption is observed.
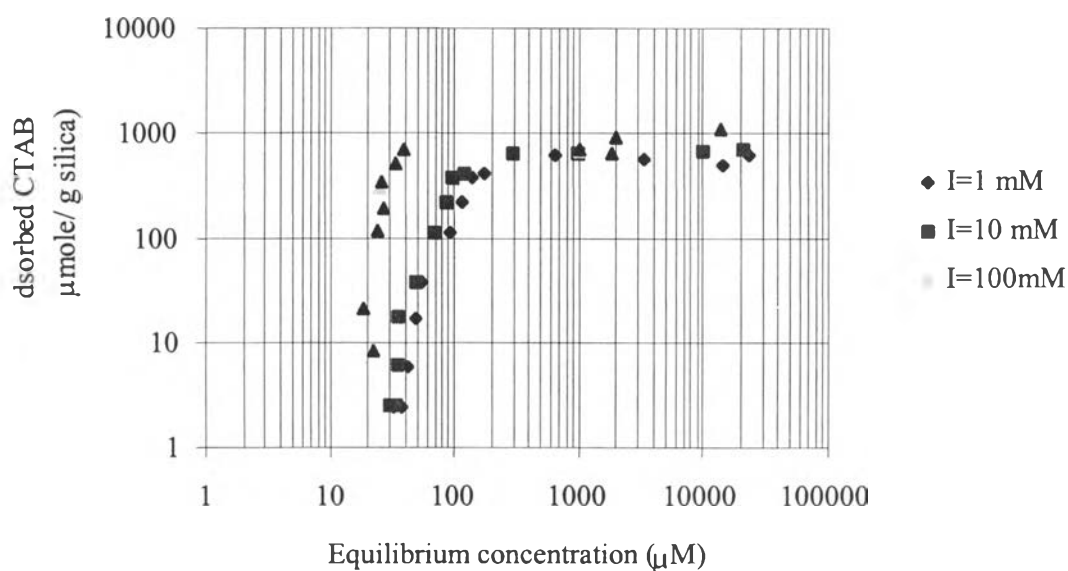

Figure 4.2 Adsorption isotherms of CTAB at pH 5 and I = 1, 10, and 100 mM.

It can also be seen from Fig. 4.2 that increasing ionic strength of the system also causes a reduction in the critical micelle concentration (CMC) of CTAB

adsorbed on silica. For pH 5, CMC was lower from approximately 900 μM without addition of NaBr to 700, 600, and 500 μM at I = 1, 10, and 100 mM, respectively.

Figure 4.3 shows CTAB adsorption isotherm at pH 8 and ionic strengths (I) of 1 and 10 mM. The CTAB adsorption was also performed at ionic strength of 100 mM of NaBr but precipitation was observed in some of the experiments, particularly at high CTAB concentration. Not having a complete set of data, it was then decided not to include the experimental data at I = 100 mM for pH 8. From Fig.4.3, it can be seen obviously that the adsorption level increases with increasing ionic strength in the solution, quite similar to the results obtained at pH 5. The CTAB adsorption at I = 10 mM is higher than the adsorption at I = 1 mM at any equilibrium CTAB concentration in the aqueous solution. Similar explanation to the studies at pH 5 can be offered to the results observed here. A reduction of the repulsion between head group of the cationic surfactant (CTAB) as a result of increasing ionic strength obviously causes higher CTAB adsorption on the silica surface. From these results, CTAB adsorbed on silica surface at higher ionic strength can be expected to be more tightly packed than those adsorbed at lower ionic strength (Atkin *et al.*, 2001).
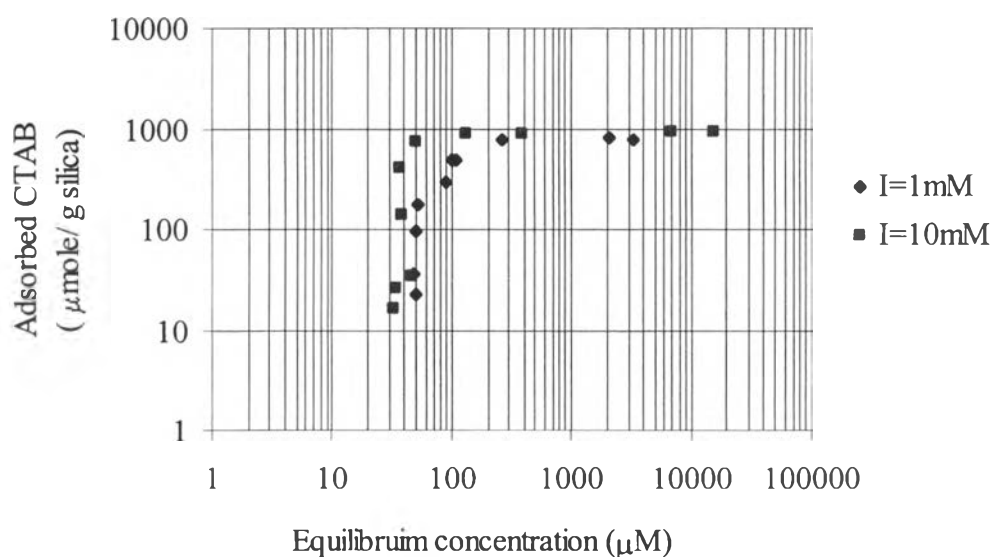

Figure 4.3 Adsorption isotherms of CTAB at pH 8 and I = 1 and 10 mM.

4.2 Adsolubilization Studies

In this part of the study, the adsolubilization of two selected organic solutes, toluene and acetophenone, into adsorbed CTAB on silica has been performed in two distinct systems, single- and mixed-solute systems. First the equilibrium CTAB adsorption on precipitated silica was carried out at a previously determined equilibrium CTAB concentration in the aqueous solution which does not exceed the CMC of the system at particular ionic strength of interest. The organic solute was then added to the equilibrium system described above by the syringe injection into the crimp-sealed vial.

4.2.1 Single-Solute System

4.2.1.1 Adsolubilization of toluene

The adsolubilization capacity of CTAB adsorbed on the silica surface for toluene was investigated by using a two-step process that was a surfactant adsorption with a subsequent adsolubilization of the organic solute. For the adsolubilization of toluene in the single-solute system, after equilibrium adsorption of CTAB on silica surface, toluene was added to the CTAB adsorbed 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 4.4 shows the adsolubilization of toluene as a function of the equilibrium concentration of toluene in the aqueous phase at pH 5 and various ionic strengths (0, 1, 10, 100 mM). For clarification, the ionic strength of 0 is referred to the system without the addition of NaBr. The adsolubilization of toluene increases with increasing equilibrium concentration of toluene. Comparing the adsolubilization of toluene at different ionic strength values clearly reveals that the adsolubilization of toluene increases with increasing ionic strength of the system. The effect is markedly seen when the ionic strength is increased from 10 mM to 100 mM. The increase in the toluene adsolubilization observed here can be related to the increased adsorption of CTAB on silica and the core volume of the admicelle for toluene adsolubilization as ionic strength is increased as seen in Fig. 4.2.
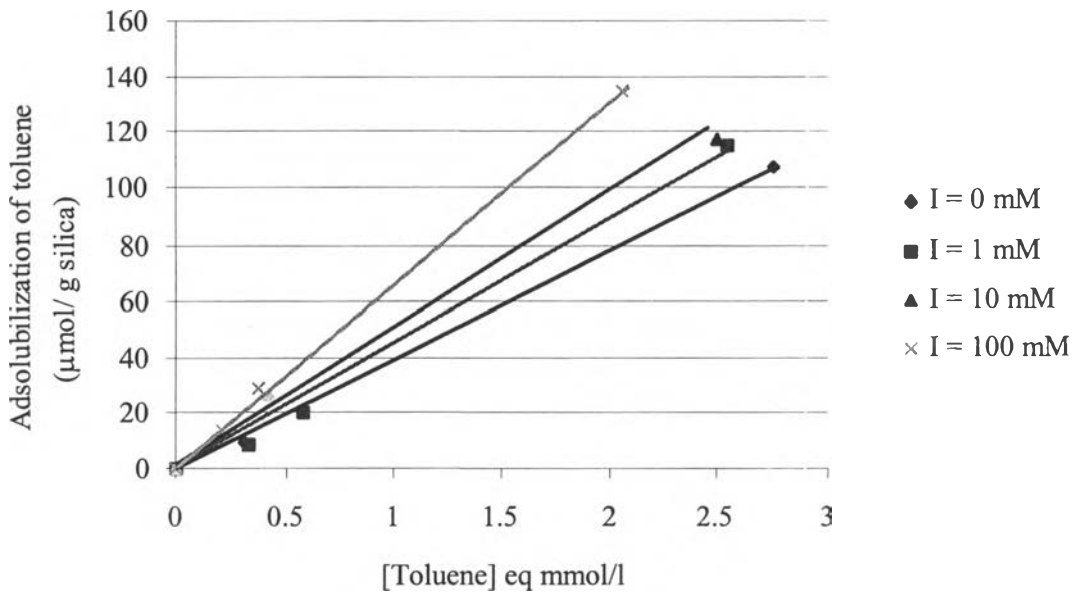
Figure 4.4 Adsolubilization of toluene at pH 5 and I = 0, 1, 10 and 100 mM.

Figure 4.5 is the plot of the partition coefficient (K) versus the mole fraction of toluene in admicelle ($X_{admicelle}$) at pH 5 and various ionic strengths (0, 1, 10 and 100 mM). The opposite trend to Fig. 4.4 is observed here. The partition coefficient calculated from the toluene adsolubilization decreases with increasing $X_{admicelle}$ in the range studied (0 to 0.35). The comparison of the partition coefficients of toluene adsolubilization at different ionic strengths ranging from 0 to 100 mM shows that the partition coefficient of toluene decreases with increasing ionic strength of the system, especially at the highest ionic strength studied for pH 5 (100 mM). This can be attributed to the properties of toluene and the structural characteristics of the adsorbed CTAB on silica at higher ionic strength (Behrends and Herrmann, 1998). Since 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 (Pradubmook, 2000). As ionic strength of the system increases, the adsorption of CTAB on silica surface increases as well the core volume of admicelle, which results in higher toluene uptake as seen in Fig. 4.4. However, the results from the partition coefficient (Fig. 4.5) reveal that the adsorbed CTAB on silica surface at higher ionic strength has lower adsolubilization capacity for toluene. Although more toluene can be adsolubilized, but the amount of toluene adsolubilized is not proportional to the

amount of adsorbed CTAB available on the silica surface, leading to a smaller $X_{admicelle}$. Since the partition coefficient (K) is defined as $X_{admicelle}$ divided by X_{bulk}, K of the toluene adsolubilization is lower when ionic strength increases.
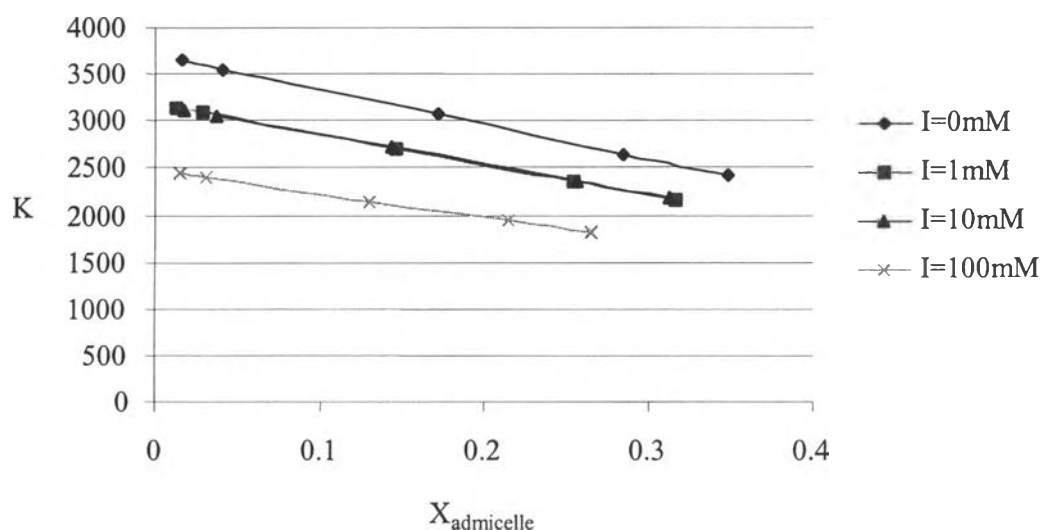

Figure 4.5 Partition coefficient (K) of toluene at pH 5 and I = 0, 1, 10 and 100 mM.

Figure 4.6 shows the plot of adsolubilization of toluene versus the equilibrium concentration of toluene at pH 8 and various ionic strengths (0, 1 and 10 mM). From this figure, it can be seen that the adsolubilization of toluene increases with increasing equilibrium concentration of toluene in a similar pattern to that observed in the system at pH 5 (Fig. 4.4). The comparison of adsolubilization of toluene at various ionic strengths shows that the adsolubilization of toluene at I = 10 mM is higher than I = 0, 1 mM at any equilibrium toluene concentration of toluene. This is essentially due to an increased adsorption of CTAB on silica surface at higher ionic strength, as shown in Figure 4.3.

Figure 4.7 shows the plot of the partition coefficient (K) versus the mole fraction of toluene in admicelle ($X_{admicelle}$) at pH 8 and various ionic strengths (0, 1 and 10 mM). Similar results to those observed in Fig. 4.5 (pH 5) can be seen here where the partition coefficient of toluene adsolubilization decreases as

the mole fraction of toluene in the admicelle increases with the same reason described previously.
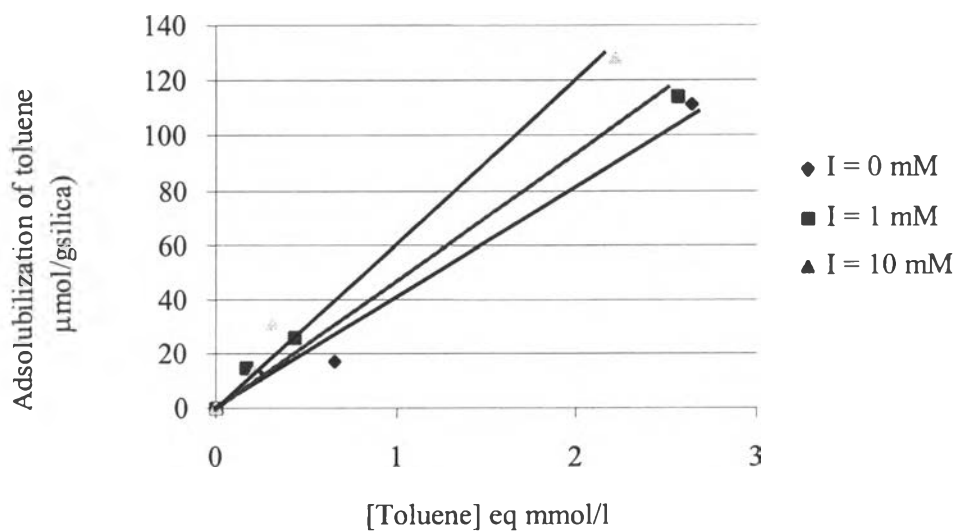

Figure 4.6 Adsolubilization of toluene at pH 8 and I = 0, 1 and 10 mM.
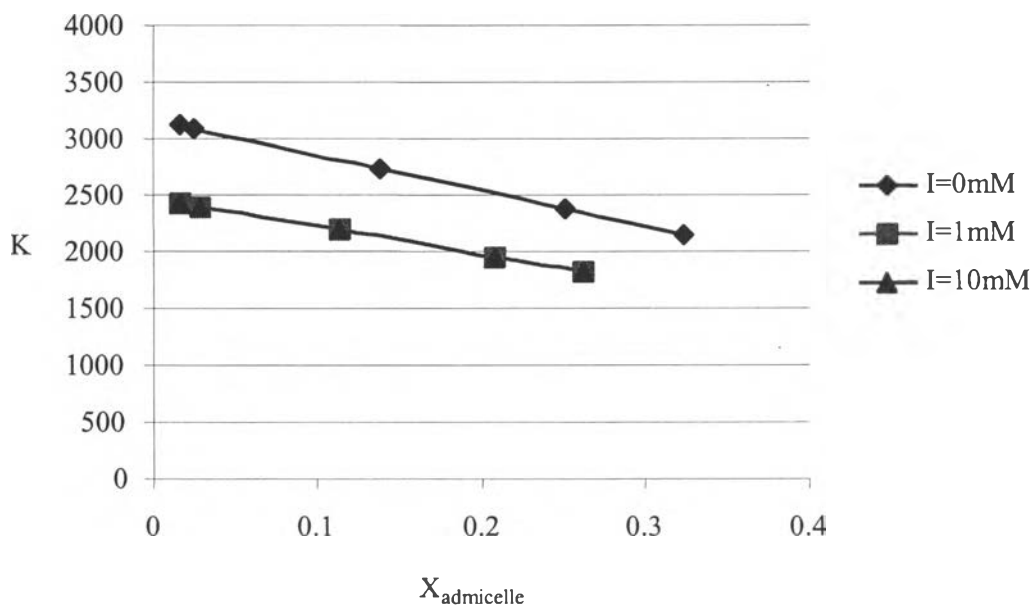

Figure 4.7 Partition coefficient (K) of toluene at pH 8 and I = 0, 1 and 10 mM.

Figure 4.8 shows the comparison of toluene adsolubilization at two different pH values (5 and 8) and a fixed ionic strength of 10 mM for both systems. As expected, the comparison shows that the adsolubilization of toluene at pH 8 is higher than the adsolubilization of toluene at pH 5 at any equilibrium toluene concentration which is basically due to the higher plateau level of CTAB adsorption on silica surface at pH 8. This can be confirmed by comparing the CTAB adsorption on silica at pH 5 and 8 and ionic strength of 10 mM (Fig. 4.2 and Fig. 4.3).
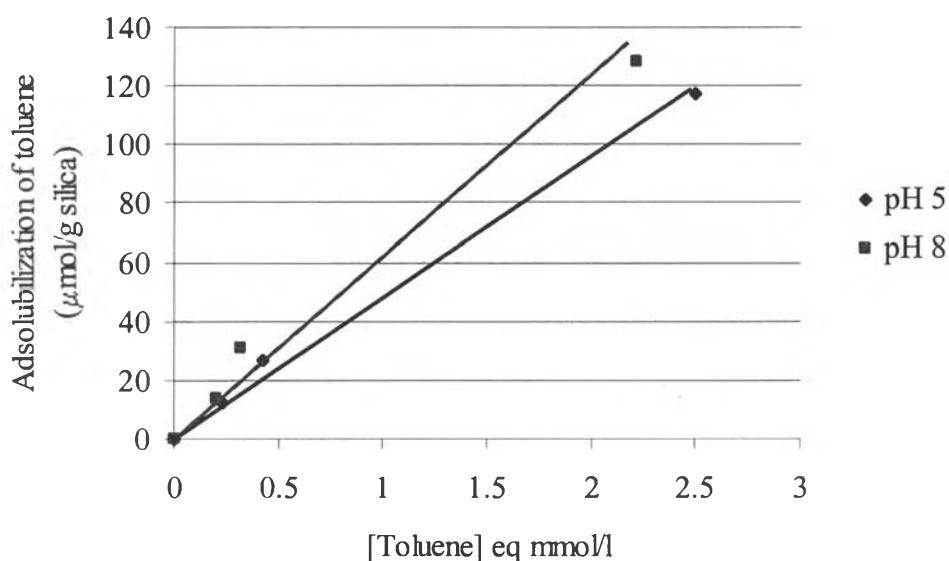
Figure 4.8 Adsolubilization of toluene at pH 5 and pH 8, I = 10 mM.

Figure 4.9 shows the partition coefficient (K) of toluene adsolubilization at pH 5 and pH 8 and a fixed ionic strength of 10 mM. It can be seen that the partition coefficient of toluene adsolubilization at pH 8 is lower than the value at pH 5 at any mole fraction of toluene in admicelle ($X_{admicelle}$). Knowing that higher level of CTAB adsorption on silica surface is obtained at pH 8, this indicates that the adsorbed CTAB on silica at high ionic strength has lower adsolubilization capacity for toluene. This may be a result of a very tightly packing with a screening effect from counterions surrounding the adsorbed CTAB molecules on silica surface.
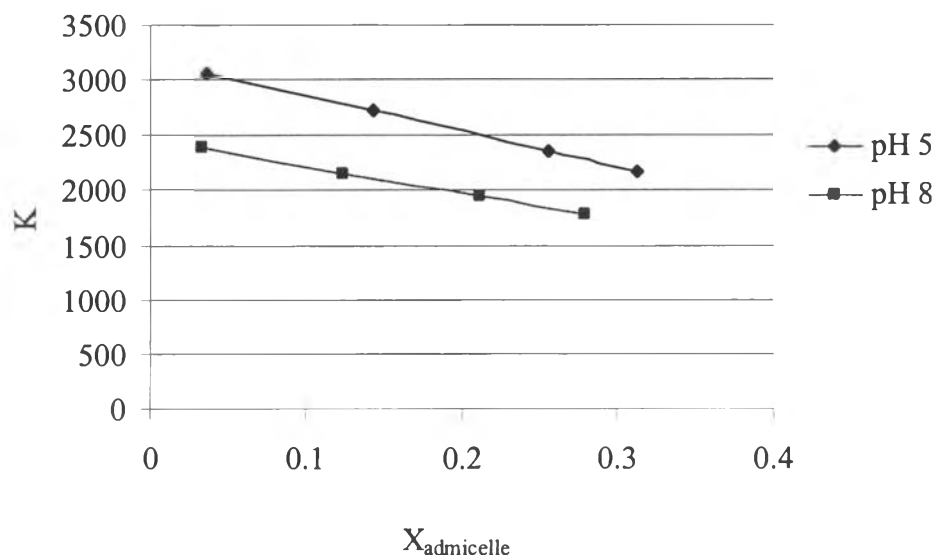
Figure 4.9 Partition coefficient (K) of toluene at pH 5 and pH 8, I = 10 mM.

4.2.1.2 Adsolubilization of acetophenone

Figure 4.10 shows the plot of acetophenone adsolubilization versus the bulk equilibrium concentration of acetophenone at pH 5 and various ionic strengths (0, 1, 10, and 100 mM). As expected, the adsolubilization of acetophenone increases with increasing acetophenone equilibrium concentration in the bulk. From the comparison between the adsolubilization of acetophenone at different ionic strengths, one can see that the adsolubilization of acetophenone increases with increasing ionic strength of the system. At I = 100 mM, the adsolubilization of acetophenone is significantly higher than at I = 0, 1, and 10 mM. This is due to an increased level adsorption of CTAB on silica surface at higher ionic strength, especially at 100 mM, as shown in Figure 4.2, which results from a reduced repulsion between like charge head groups of the adsorbed surfactant.

The plot between the partition coefficient (K) and the mole fraction of acetophenone in the admicelle ($X_{admicelle}$) is shown in Figure 4.11. It can be seen that the partition coefficient dramatically decreases in the range of $X_{admicelle} = 0$ to 0.05 and then becomes quite constant in the range of $X_{admicelle} = 0.05$ to 0.15.

The results shown here exhibit a similar trend as observed in our previous study (Pradubmook, 2000). In contrast to the case of toluene adsolubilization, the partition
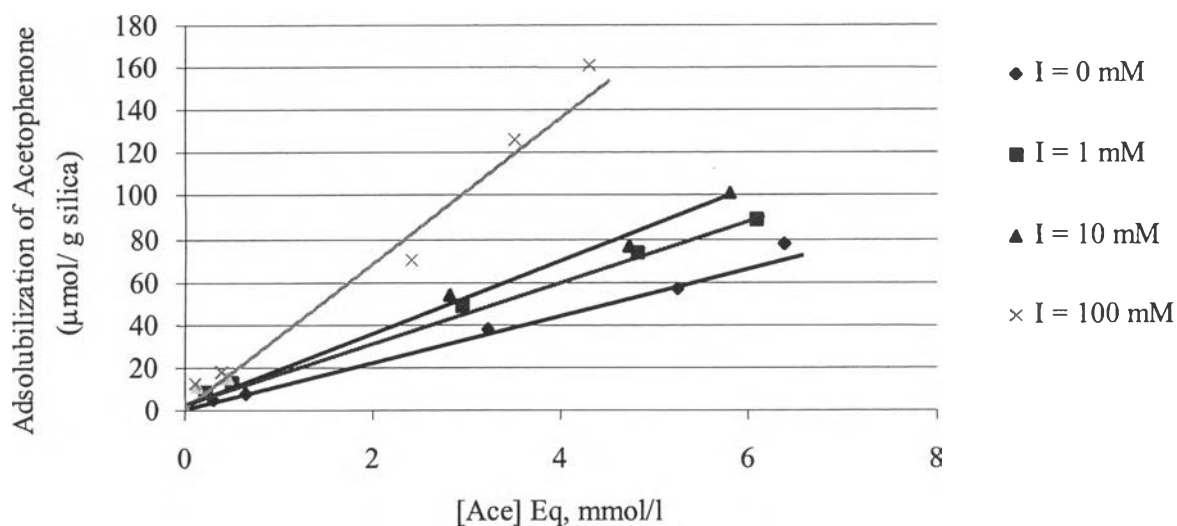

Figure 4.10 Adsolubilization of acetophenone at pH 5 and I = 0, 1, 10, and 100 mM.
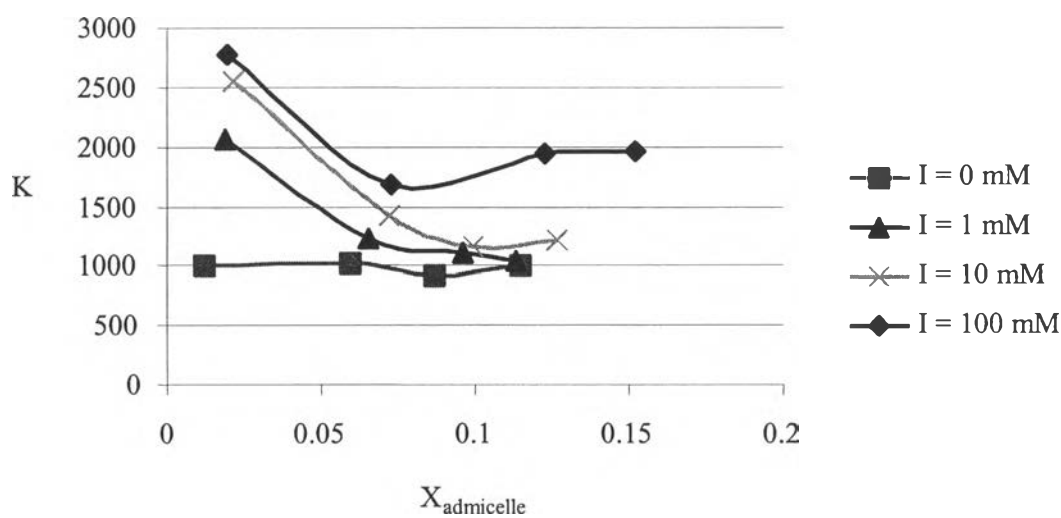

Figure 4.11 Partition coefficient (K) of acetophenone at pH 5 and I = 0, 1, 10, and 100 mM.

coefficient of acetophenone adsolubilization increases with increasing ionic strength of the system. The adsolubilization of acetophenone appears to be proportional to the adsorbed CTAB available on the silica surface. This can be attributed to a highly polar in nature of acetophenone, whose dipole moment is 10 times higher than toluene's, and thus, it is expected that acetophenone adsolubilizes primarily into the head group and palisade region of the admicelle (Rouse *et al.*, 1995; Kitiyanan *et al.*, 1996; Pradubmook, 2001).

Figure 4.12 shows the plot of acetophenone adsolubilization versus the bulk equilibrium concentration of acetophenone at pH 8 and various ionic strengths (0, 1, and 10 mM). The results are very similar to those obtained at pH 5. The adsolubilization of acetophenone increases with increasing acetophenone equilibrium concentration. When compared at various ionic strengths, acetophenone adsolubilization is higher at higher ionic strength. Figure 4.13 shows the partition coefficient as a function of mole fraction of acetophenone in the admicelle. The partition coefficient dramatically decreases in a low range of $X_{admicelle}$ and then levels off. The partition coefficient of acetophenone adsolubilization is higher at higher ionic strength as observed in the adsolubilization at pH 5.
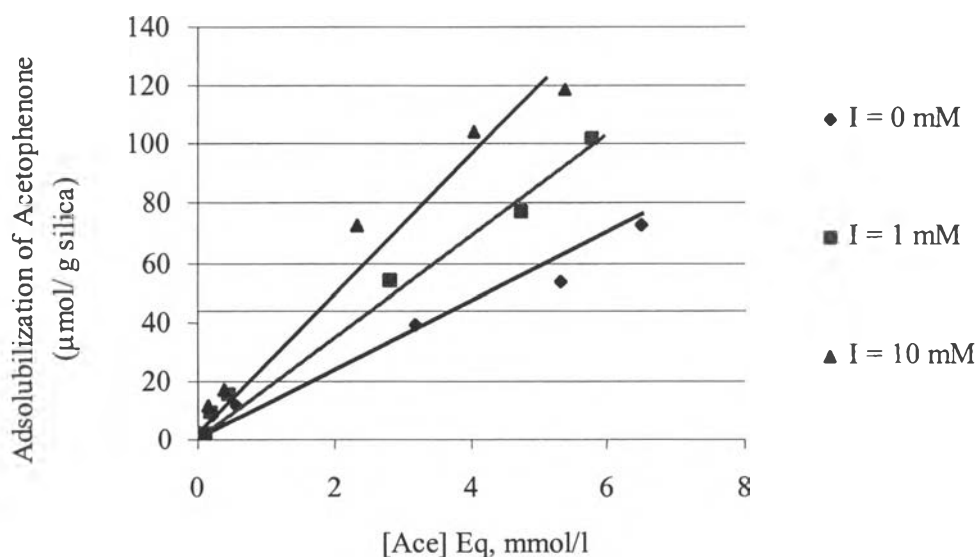

Figure 4.12 Adsolubilization of acetophenone at pH 8 and I = 0, 1, and 10 mM.
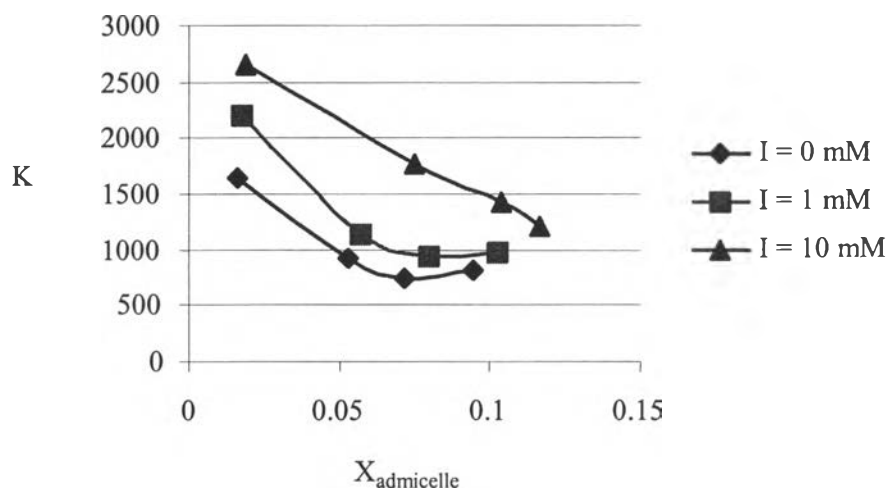
Figure 4.13 Partition coefficient (K) of acetophenone at pH 8 and I = 0, 1, and
10 mM.

Figure 4.14 shows the adsolubilization of acetophenone versus the bulk equilibrium concentration of acetophenone at two pH values (5 and 8) and a fixed ionic strength of 10 mM. As expected, the adsolubilization of acetophenone increases with increasing acetophenone equilibrium concentration. From the comparison between the adsolubilization of acetophenone at pH 5 and pH 8, the adsolubilization of acetophenone at pH 8 is significantly higher than the adsolubilization of acetophenone at pH 5. The amount of adsolubilized acetophenone at pH 8 is approximately 1.5 times that at pH 5, which is probably due to the increase in CTAB adsorption and an increase in the polarity of the admicelle.

The plot between the partition coefficient (K) of acetophenone and the mole fraction of acetophenone in the admicelle ($X_{admicelle}$) at pH 5 and pH 8 and a fixed ionic strength of 10 mM is shown in Figure 4.15. As can be seen, the partition coefficient dramatically decreases with increasing $X_{admicelle}$ and the partition coefficient at pH 8 is higher than that at pH 5. In contrast to toluene, acetophenone can adsolubilize into the head group as well as the palisade regions of the admicelle as previously described.
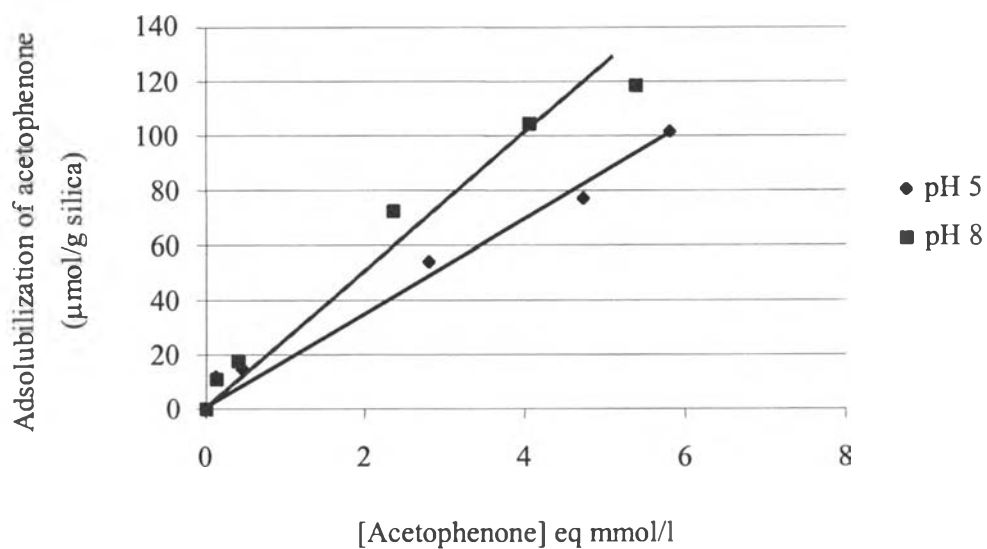
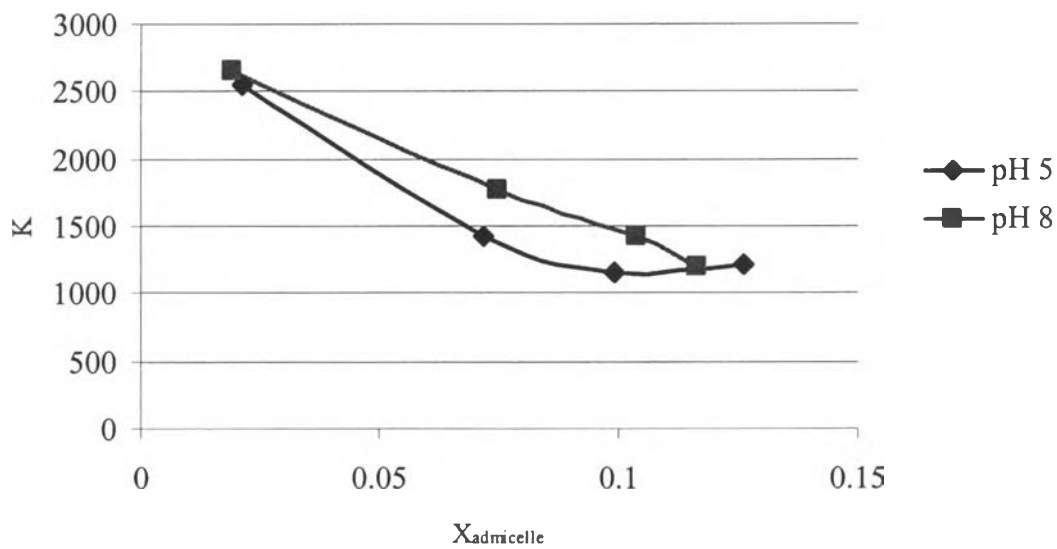**Figure 4.14** Adsolubilization of acetophenone at pH 5 and 8, I = 10 mM.

Figure 4.15 Partition coefficient (K) of acetophenone at pH 5 and 8 and

I = 10 mM.

4.2.2 Mixed-Solute Systems

4.2.2.1 Adsolubilization of toluene in the presence of acetophenone

Figures 4.16 and 4.17 show the plots of toluene adsolubilization versus equilibrium concentration of toluene in the presence of added acetophenone, at pH 5 and pH 8, respectively, and under various ionic strengths. From both figures, it can be seen that toluene adsolubilization increases slightly with increasing ionic strength of the system. When compared with the toluene adsolubilization in single-solute system, the toluene adsolubilization is slightly higher in the presence of acetophenone (mixed-solute system). Although not significant, one possible reason for this effect is that the presence of acetophenone in the palisade layer displaces water molecules that would normally be in the palisade region, resulting in an increase in the core volume of the admicelle and thus more toluene can then be adsolubilized.
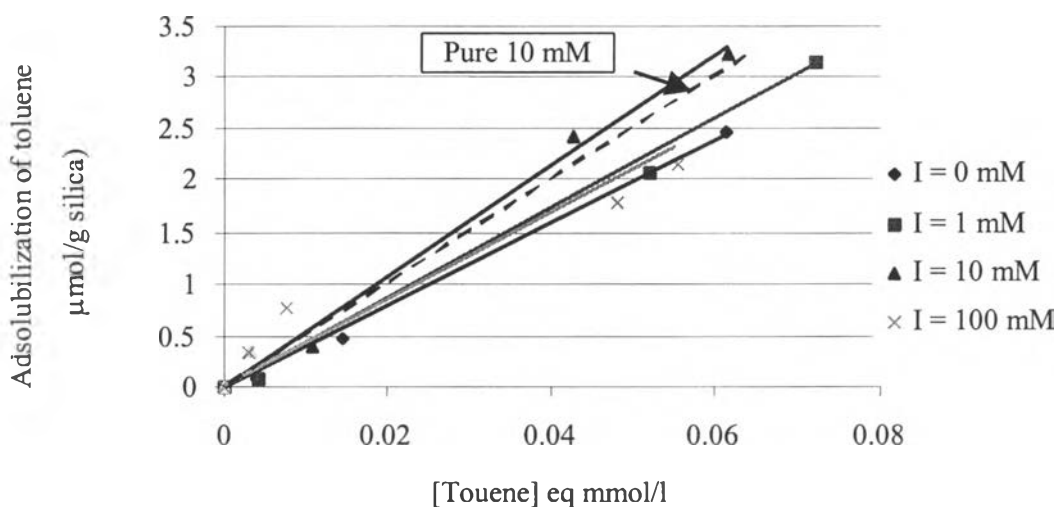

Figure 4.16 Adsolubilization of toluene in the presence of acetophenone at pH 5 and I = 0, 1, 10, and 100 mM.
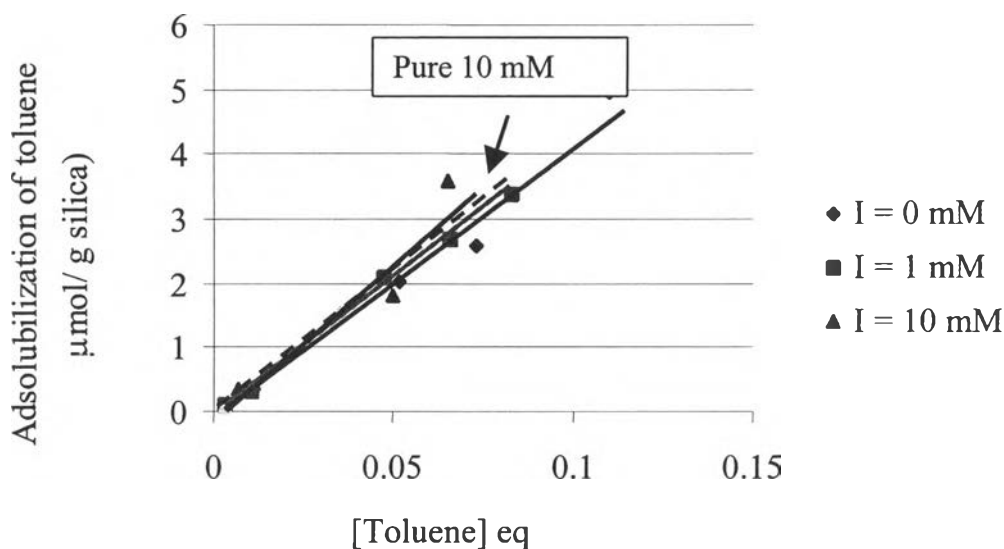
Figure 4.17 Adsolubilization of toluene in the presence of acetophenone at pH 8 and I = 0, 1 and 10 mM.

Figures 4.18 and 4.19 show the partition coefficient (K) of toluene versus the mole fraction of toluene in admicelle ($X_{admicelle}$) at pH 5 and pH 8, respectively, and under various ionic strengths. In the $X_{admicelle}$ range shown in these figures (0.1-0.4 mM^{-1}), the partition coefficient of toluene in the presence of acetophenone is quite constant as $X_{admicelle}$ increases. A slight decrease in K with increasing $X_{admicelle}$ is observed particularly at high ionic strength (e.g., 10 mM) for pH 8. The comparison of the partition coefficients between different ionic strengths indicates that the partition coefficient of toluene in the presence of acetophenone slightly increases with increasing ionic strength. When compared to the pure system of toluene, the presence of acetophenone in the system enhance the adsolubilization of toluene into the admicelle. As explained earlier, the presence of acetophenone in the palisade layer may displaces water molecules that would normally be in the palisade region, resulting in an increase in the core volume of the admicelle and thus more toluene can be adsolubilized.
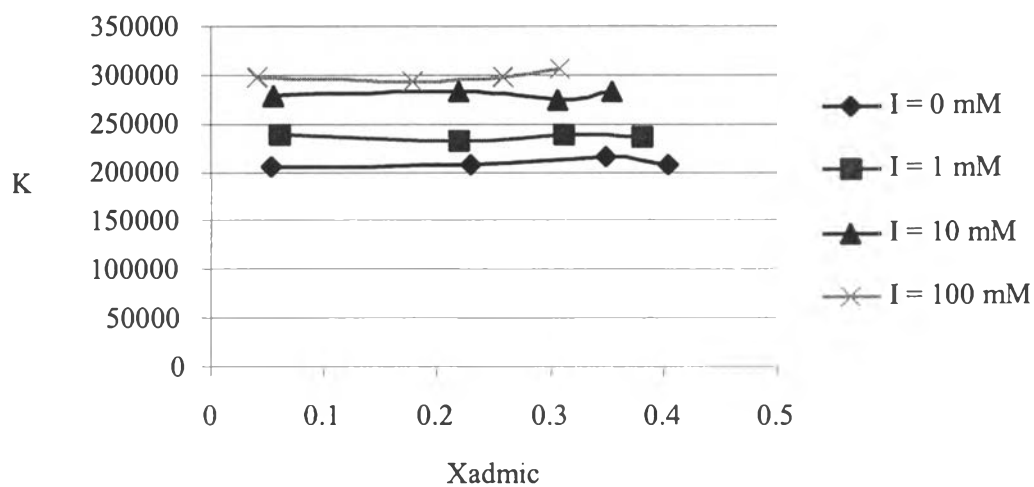
Figure 4.18 Partition coefficient (K) of toluene in the presence of acetophenone at pH 5 and I = 0, 1, 10, 100 mM.
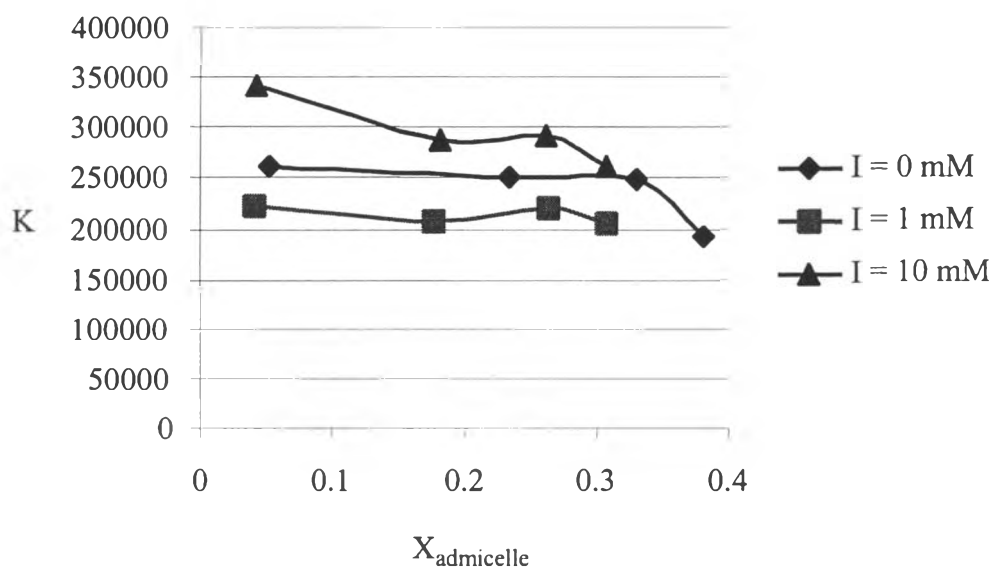

Figure 4.19 Partition coefficient (K) of toluene in the presence of acetophenone at pH 8 and I = 0, 1 and 10 mM.

4.2.2.2 Adsolubilization of acetophenone in the presence of toluene

Figures 4.20 and 4.21 show the acetophenone adsolubilization versus the equilibrium concentration of acetophenone in the presence of added toluene at pH 5 and pH 8, respectively, and under various ionic strengths. Similar to the systems with acetophenone alone (Fig. 4.10 and 4.12), the adsolubilization of acetophenone increases significantly as ionic strength increases. This appears to be a result of an increase in the adsorption of CTAB at higher ionic strength as described in the previous section. When compared the results at the same ionic strength (10 mM), it is obvious that the acetophenone adsolubilization is higher in the presence of toluene for both pH values. At pH 5 and I = 10 mM, the amount of adsolubilized acetophenone in the presence of toluene is approximately 1.5 times that of the pure acetophenone system. At pH 8 and I = 10 mM, the amount of adsolubilized acetophenone is approximately 3 times that of the pure acetophenone system. This synergetic effect has also been observed in the previous study in the absence of ionic strength (Pradubmook, 2000). A possible explanation is that toluene in the the core swell the bilayer, loosening the molecules in the palisade layer, thus providing more
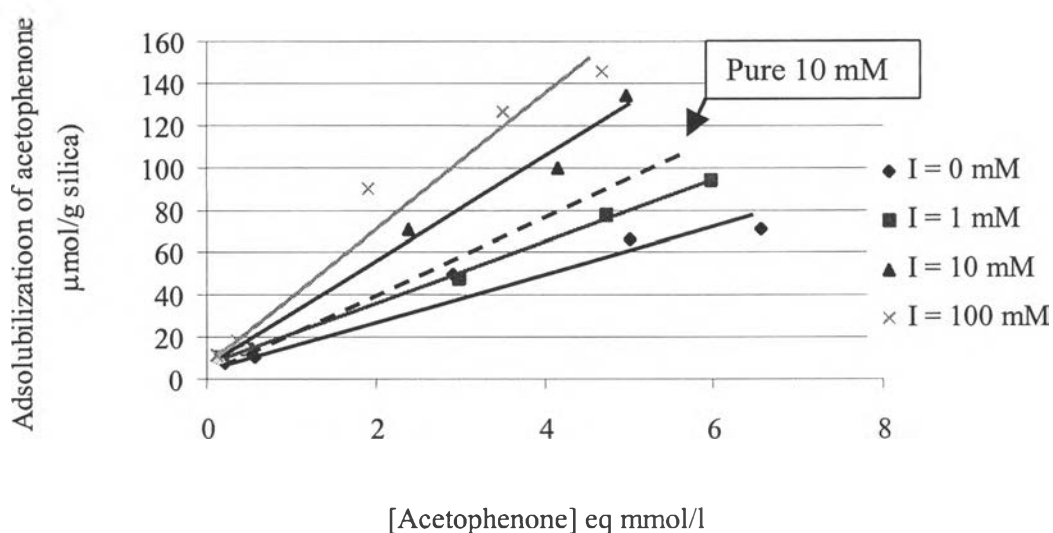

Figure 4.20 Adsolubilization of acetophenone in the presence of toluene at pH 5 and
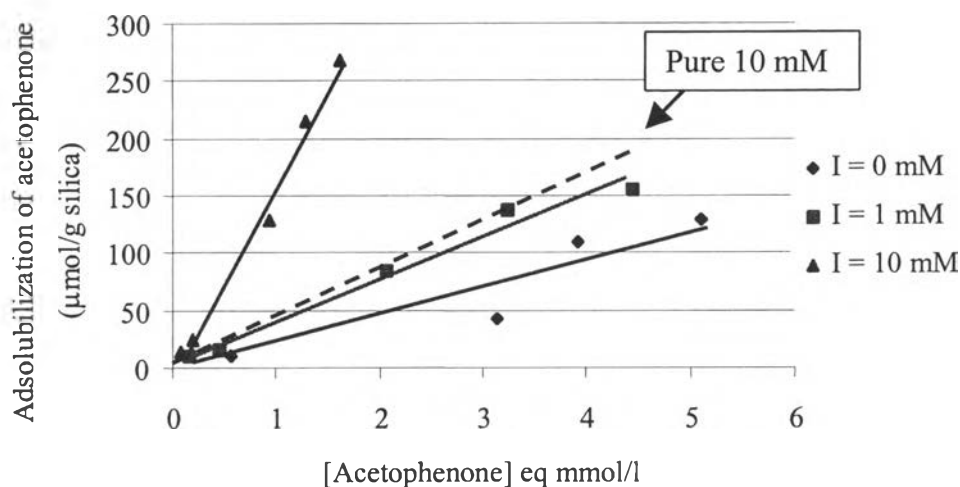I = 0, 1, 10, 100 mM.

Figure 4.21 Adsolubilization of acetophenone in the presence of toluene at pH 8 and
I = 0, 1 and 10 mM.

volume for acetophenone to adsolubilize. Additionally, the hydrophobic interaction
between both adsolibilizates may also result in higher acetophenone adsolubilization
in the presence of toluene (co-solute effect).

Figure 4.22 shows the partition coefficient (K) of
acetophenone versus the mole fraction of acetophenone in admicelle ($X_{admicelle}$) in the
presence of toluene at pH 5 and various ionic strengths (0, 1, 10, and 100 mM).
Similar to the single-solute system (Fig. 4.11), the partition coefficient in mixed-
solute system at pH 5 decreases with increasing the mole fraction of acetophenone in
admicelle. As acetophenone partitions primarily into the palisade region,
competition for available sites/space increases with increasing level of
adsolubilization. When compared at different ionic strengths, the partition
coefficient increase as ionic strength of the system increases. This can be attributed
to the increase CTAB adsorption at higher ionic strength and the fact that
acetophenone is highly polar and thus more acetophenone can adsolubilize into the
palisade region of the admicelle. Figure 4.23 shows the partition coefficient (K)
versus the mole fraction of acetophenone in admicelle in the presence of toluene at
pH 8 and various ionic strengths (0, 1, 10 mM). At this pH value, the partition
coefficient varies insignificantly with $X_{admicelle}$, in fact, the coefficient is quite

constant in the range of $X_{admicelle}$ studied. However, the effect of ionic strength on the partition coefficient appears to be the same as observed at lower pH value (pH 5).
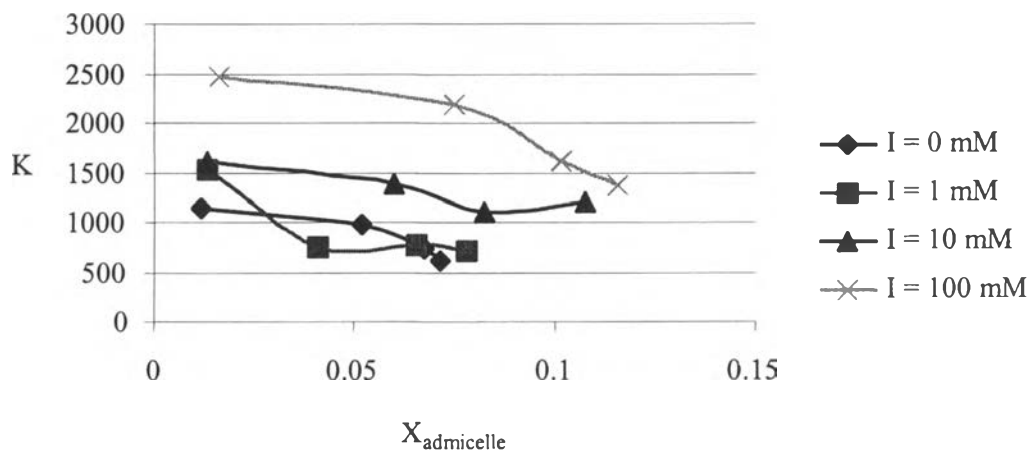

Figure 4.22 Partition coefficient (K) of acetophenone in the presence of toluene at pH 5 and I = 0, 1, 10, and 100 mM.
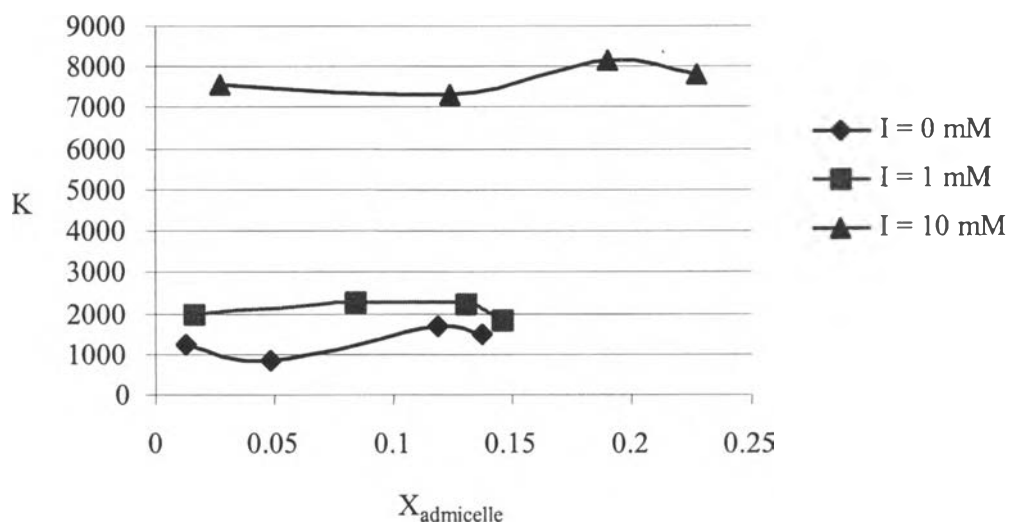

Figure 4.23 Partition coefficient (K) of acetophenone in the presence of toluene at pH 8 and I = 0, 1 and 10 mM.