

CHAPTER IV

RESULTS AND DISCUSSION

4.1 CTAB Adsorption on Hi-Sil 255

The adsorption of CTAB on Hi-Sil 255 silica was performed at two pH values (5 and 8) and the adsorption isotherms constructed. Adsorption levels determined from this portion of the study will be examined to determine feed conditions needed for the subsequent adsolubilization studies.

4.1.1 CTAB Adsorption Isotherms

Figure 4.1 shows the adsorption isotherms at pH 5 and 8 and ionic strength (I) 10 mM plotted on a log-log scale. From this figure, we can see that for every equilibrium concentration, CTAB adsorption on Hi-Sil 255 silica at pH 8 is higher than at pH 5. The plateau (maximum) CTAB adsorption on silica at pH 5 and pH 8 ionic strength (I=10mM) are approximately 700 and 900 $\mu\text{moles/g}$ silica, respectively. This higher degree of adsorption is primarily attributed to two factors. First, the surface of the silica becomes more negatively charged the farther pH is from the point of zero charge (PZC) of the silica which is pH 2-3. Second, the repulsion between head groups of cationic surfactant (CTAB) is reduced by counterion adsorption (Br^-) at increasing ionic strength (Behrends and Herrmann, 1998).

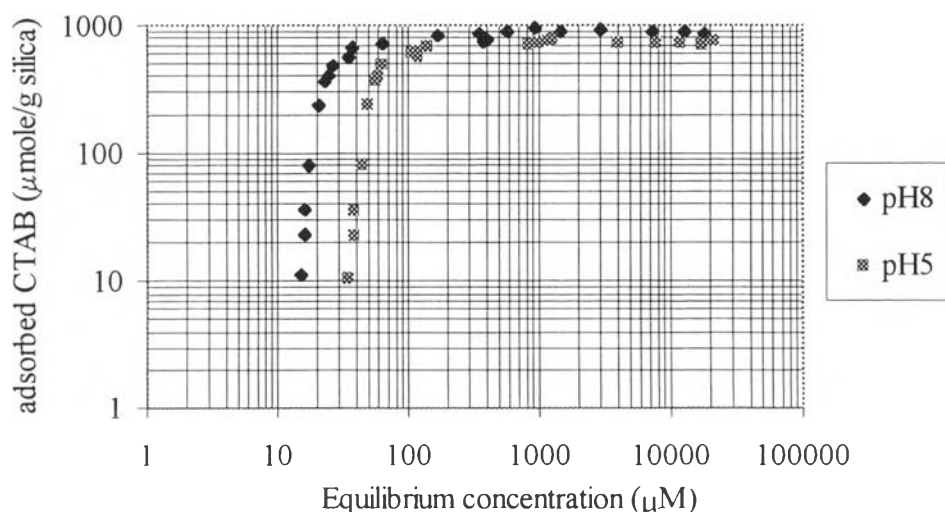


Figure 4.1 Adsorption isotherms of CTAB at pH 5 and 8 and ionic strength 10 mM.

4.1.2 Different Surface Adsorption Regions Based on CTAB Equilibrium Concentration

For each pH three points were chosen, one each in regions I, II and III of the standard adsorption isotherm. (Figure 4.1). This corresponds to three equilibrium concentrations / adsorption levels of CTAB (low, medium, and high but below the plateau). Table 4-1A shows the amount of CTAB adsorbed on Hi-Sil 255 at the three levels at pH 5 while Table 4-1B shows the amount of CTAB adsorbed on Hi-Sil 255 at pH 8. In each region, surface adsorption on silica for both pHs were found to be quite similar. This resulted from an attentive experimental design by carefully controlling the initial CTAB concentration such that the equilibrium concentration and adsorbed amount were reproducible as determined by using Total Organic Carbon (TOC), Elemental Analyzer (EA) or both.

Table 4-1A The amount of CTAB adsorbed on Hi-Sil 255 at pH 5.

Region	Initial (μM)	C_{eq}^* (μM)	Adsorbed CTAB [#] ($\mu\text{mole/ g silica}$)
I	600	39.15	22.43
II	9000	57.55	357.70
III	17000	141.01	674.24

Table 4-1B The amount of CTAB adsorbed on Hi-Sil 255 at pH 8.

Region	Initial (μM)	C_{eq}^* (μM)	Adsorbed CTAB [#] ($\mu\text{mole/ g silica}$)
I	600	16.27	23.35
II	9000	23.45	359.06
III	18000	63.47	717.46

* Determined by using TOC

Determined by using TOC and EA (average values)

4.2 Adsolubilization Studies

Next, the adsolubilization of toluene and acetophenone into the adsorbed CTAB aggregates at different adsorption levels was determined, both for 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 was different for each region. The organic solute was then added to the equilibrium system described above by syringe injection into the crimp-sealed vial. The amount of solute used was carefully controlled to be within its aqueous solubility limit; 542 ppm and 6842 ppm at 30°C for toluene and acetophenone, respectively (Yaws, 1999).

4.2.1 Single-solute systems

4.2.1.1 Adsolubilization of toluene

The adsolubilization capacity of CTAB adsorbed on silica for toluene in each region was investigated by using a two-step process which started with surfactant adsorption followed by 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 system containing CTAB adsorbed silica. After equilibrium was achieved, the concentration of toluene in the supernatant was analyzed by a headspace GC and the adsolubilized amount of toluene was determined using method of difference.

Figure 4.2 shows the plot of toluene adsolubilization versus the bulk equilibrium concentration of toluene for all three regions at pH 5. As expected, the adsolubilization of toluene increases with increasing toluene equilibrium concentration in the bulk. From the comparison between the adsolubilization of toluene at different surface adsorption levels, one can see that the adsolubilization of toluene increases with increasing amounts of adsorbed CTAB. The adsolubilized amount of toluene in region III is higher than that of regions II and I, respectively. However, the increased adsolubilized amount is not directly proportional to the increased amount of CTAB adsorbed on silica as seen in Table 4-1A.

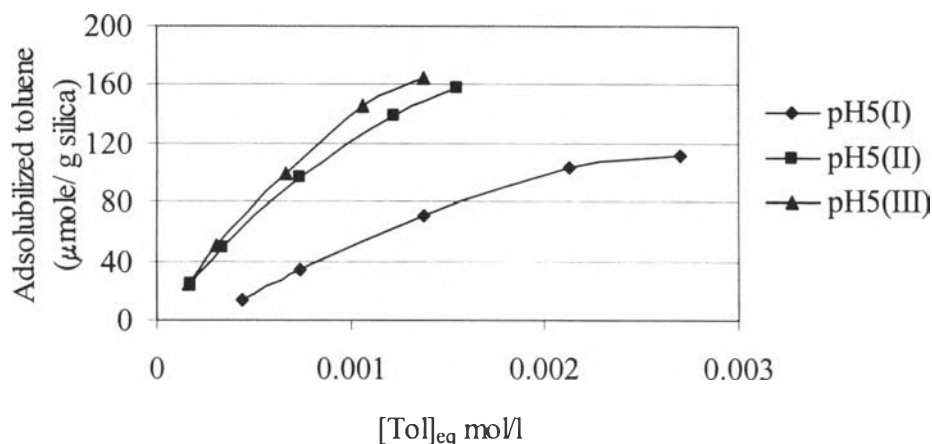


Figure 4.2 Adsolubilization of toluene in regions I, II, III at pH 5 and $I = 10$ mM.

From Table 4-1A, the amount of CTAB adsorbed on silica in region II is approximately 15 times the amount of CTAB adsorbed on silica in region I whereas Fig. 4.2 shows the amount of adsolubilized toluene in region II is only 1.5 times that of region I. Similar comparison can be done between regions II and III. From Table 4-1A, the amount of CTAB adsorbed on silica in region III is approximately 1.8 times the amount of CTAB adsorbed on silica in region II whereas Fig. 4.2 shows the amount of adsolubilized toluene in region III is only 1.2 times that of region II. The results suggest that the adsolubilization of toluene cannot only be related to the amount of CTAB adsorbed on silica but the structural arrangement of CTAB aggregates on silica in each region should also be taken into account (Behrends and Herrmann, 2000; Atkin *et al.*, 2001). Obviously, the increased amount of toluene adsolubilized into adsorbed CTAB on silica does not directly correspond to the increase in the amount of CTAB adsorbed on silica. Especially, for low and medium surfactant adsorption (regions I and II), the arrangement of CTAB on silica appears to have a greater effect on the adsolubilization of toluene than the amount of adsorbed CTAB. In contrast, when approaching high surfactant adsorption (region III), the adsolubilization of toluene seems to depend mainly on the amount of adsorbed CTAB on silica.

Figure 4.3 shows the plot of the partition coefficient (K) versus the mole fraction of toluene in admicelle ($X_{\text{admicelle}}$) at pH 5 for all three CTAB adsorption regions (I, II and III). It can be seen from this figure that for all three regions the partition coefficient for toluene decreases with increasing $X_{\text{admicelle}}$

in the studies range (0 to 0.9). Comparing the partition coefficients of toluene adsolubilization at different CTAB adsorption levels, the partition coefficient of toluene decreases with increasing the amount of CTAB adsorbed, especially at the highest amount of CTAB adsorbed (region III). This can be attributed to the properties of toluene, the amount of CTAB adsorbed and the arrangement of CTAB being adsorbed 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, 2000). As the amount of CTAB increases, the adsorption of CTAB on silica surface increases so does the core volume of the admicelle, resulting in higher toluene uptake as seen in Figure 4.2. However, the results from the partition coefficient (Figure 4.3) reveal that the adsorbed CTAB on silica at higher CTAB adsorption levels has lower adsolubilization capacity for toluene. Although more toluene can be adsolubilized into CTAB aggregates as the adsorbed CTAB amount increases, but the increased amount of adsolubilized toluene is not proportional to the increased amount of adsorbed CTAB available on the silica surface. This leads to smaller K values since the partition coefficient (K) is defined as $X_{\text{admicelle}}$ divided by X_{bulk} , K of the toluene adsolubilization is lower when the amount of CTAB increases. This is a key indication of the difference in structural arrangement of the adsorbed CTAB aggregates on silica surface between different surface adsorption at the corresponding equilibrium concentration.

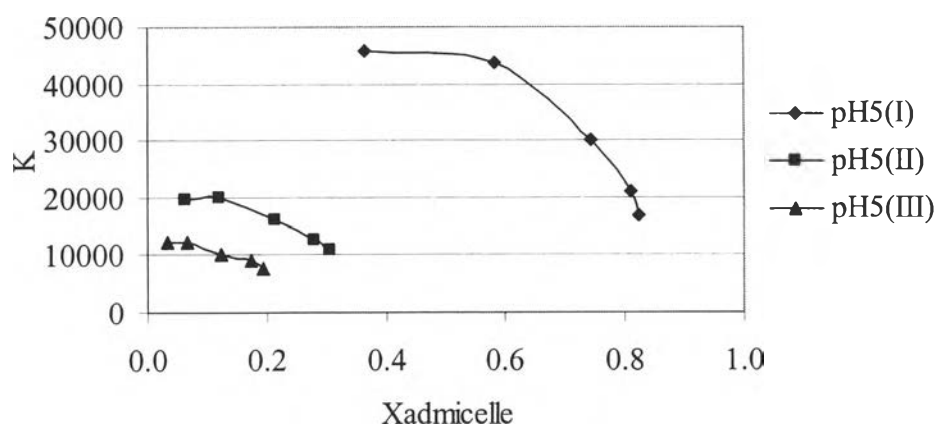


Figure 4.3 The partition coefficient (K) of toluene in regions I, II, III at pH 5 and I = 10 mM.

Figure 4.4 shows the plot of the adsolubilization of toluene versus the bulk equilibrium concentration of toluene in region I, II and III at pH 8. 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 (Figure 4.2). The comparison of the adsolubilization of toluene at different CTAB adsorption regions show that the adsolubilization of toluene at region III is higher than region II and region I at any equilibrium concentration of toluene. However, the increased adsolubilized amount is not directly proportional to the increased amount of CTAB adsorbed on silica as seen in Table 4-1B.

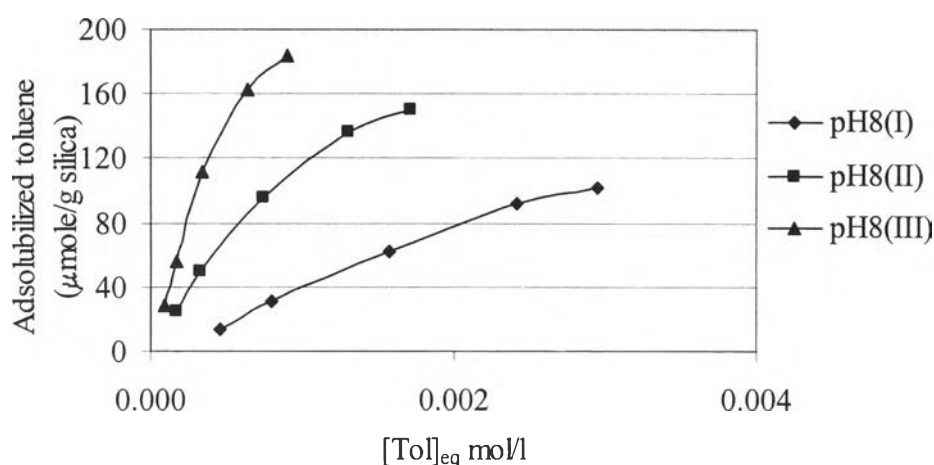


Figure 4.4 Adsolubilization of toluene in region I, II, III at pH 8 and I = 10 mM.

From Table 4-1B, the amount of CTAB adsorbed on silica in region II is approximately 15 times the amount of CTAB adsorbed on silica in region I whereas Fig. 4.4 shows the amount of adsolubilized toluene in region II is only 1.6 times that of region I. Similar comparison can be done between regions II and III. From Table 4-1B, the amount of CTAB adsorbed on silica in region III is approximately 2 times the amount of CTAB adsorbed on silica in region II whereas Fig. 4.4 shows the amount of adsolubilized toluene in region III is only 1.2 times that of region II. This is essentially due to an increase in adsorption of CTAB on silica surface at different amounts of CTAB adsorbed (Region I, II and III) and the structural arrangement of CTAB aggregates on silica in each region.

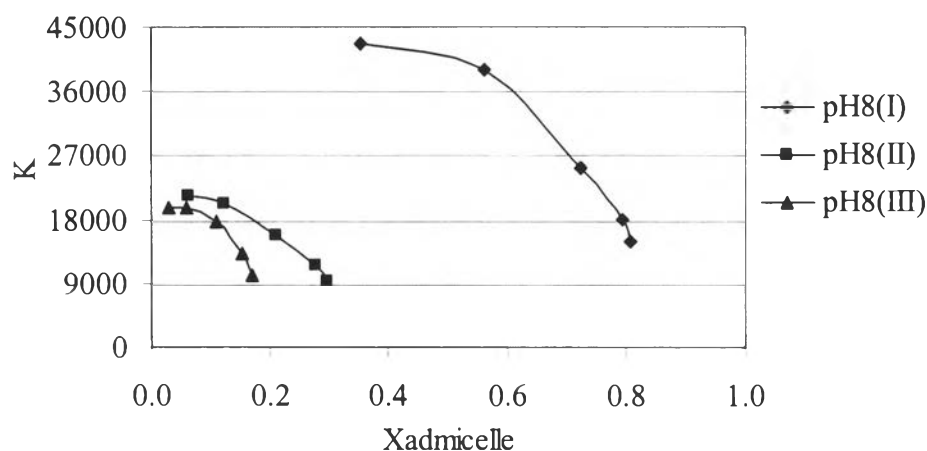


Figure 4.5 The partition coefficient (K) of toluene in region I, II, III at pH 8 and $I = 10$ mM.

Figure 4.5 shows the plot of the partition coefficient (K) versus the mole fraction of toluene in the admicelle ($X_{admicelle}$) at pH 8 and different adsorbed CTAB levels. Similar results to those observed in Figure 4.3 (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 shows the comparison of toluene adsolubilization at two different pH values (5 and 8) in three regions (I, II and III). The result in region I show that the adsolubilization of toluene into adsorbed CTAB at pH 5 is slightly higher than that of at pH 8 at any equilibrium concentration of toluene which is opposite that found in previous works which examined mostly systems with region III levels of adsorption (Behrends and Herrmann, 2000; Pradubmook, 2001). It can be confirmed that the structural arrangement of CTAB on silica appears to have strongly effect on the adsolubilization of toluene than the amount of CTAB adsorbed especially at the low amount of CTAB adsorbed. Moreover the results in region II and III can proved that the effect of the structural arrangement of CTAB aggregates on silica on the adsolubilization of toluene decrease when the amount of adsorbed CTAB increased (From region I, II, and III). From Table 4-1A and 4-1B, the amount of CTAB adsorbed on silica in region II and III of pH 8 are 1.014 and 1.064 times

that of region II and III of pH 5 whereas Fig. 4.6 shows the amount of adsorbed toluene in region II and III of pH 8 are 1.03 and 1.13 times that of region II and III at pH 5

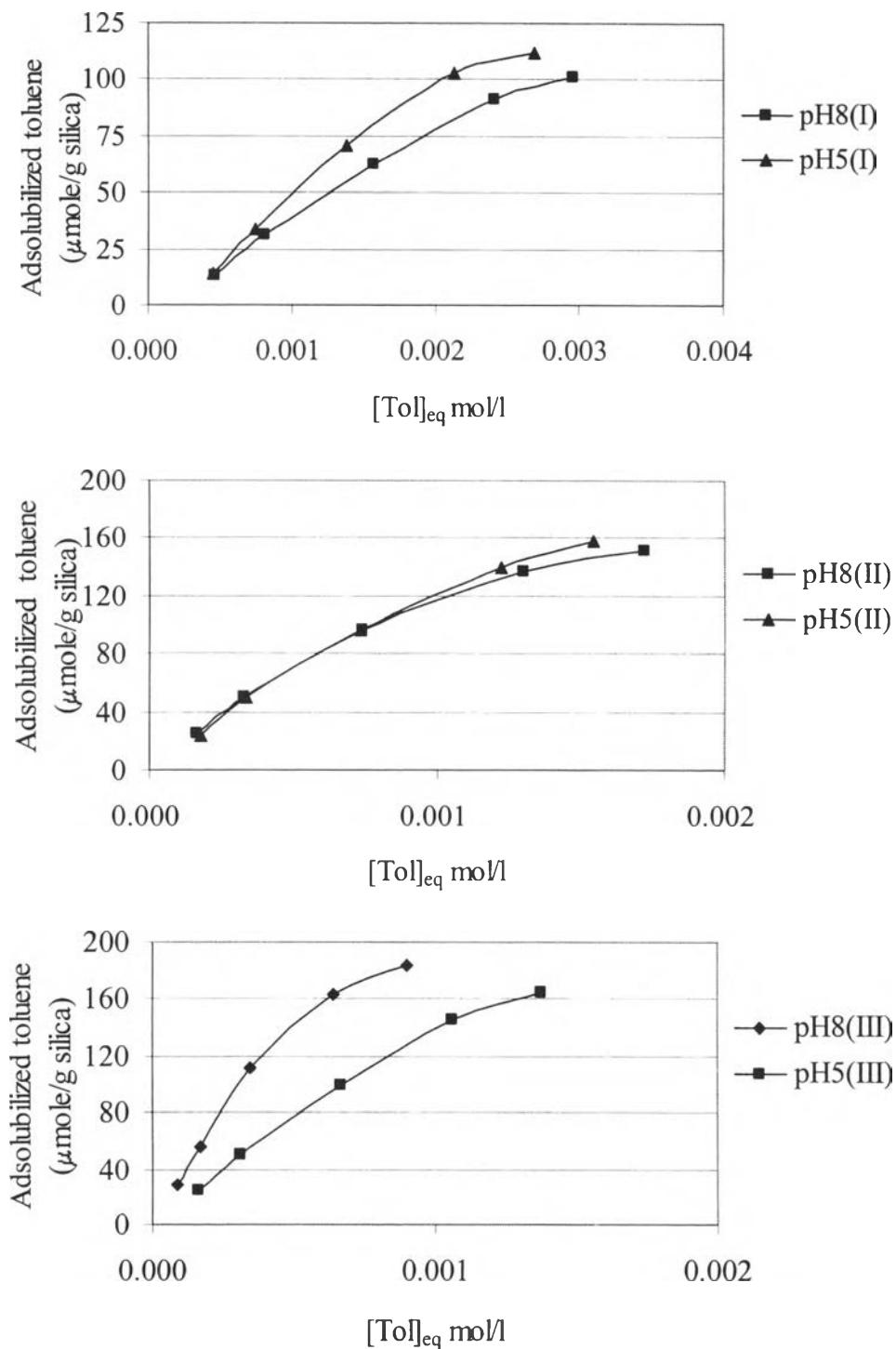


Figure 4.6 Adsolubilization of toluene in region I, II, III at pH 5 and 8 and $I = 10 \text{ mM}$.

4.2.1.2 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 (245 nm).

Figure 4.7 shows the plot of acetophenone adsolubilization versus the bulk equilibrium concentration of acetophenone for all three regions at pH 5. As expected, the adsolubilization of acetophenone increases with increasing acetophenone equilibrium concentration in the bulk phase. Comparing the adsolubilization of acetophenone at different CTAB equilibrium concentrations corresponding to different surface adsorption regions I, II, III, one can see that the adsolubilization of acetophenone increases with increasing the amount of adsorbed CTAB on silica. It can be noticed that the adsolubilization of acetophenone is not only dependant on the amount of CTAB adsorbed on silica at different CTAB equilibrium concentration. From Table 4-1A, the amount of CTAB adsorbed on silica in region II is approximately 15 times the amount of CTAB adsorbed on silica in region I whereas Fig. 4.7 shows the amount of adsolubilized acetophenone in region II is only 3 times that of region I. Similar comparison can be done between regions II and III. From Table 4-1A, the amount of CTAB adsorbed on silica in region III is approximately 1.8 times the amount of CTAB adsorbed on silica in region II whereas Fig. 4.7 shows the amount of adsolubilized acetophenone in region III is only 1.2 times that of region II. The results suggest that the adsolubilization of acetophenone cannot be related only to the amount of CTAB adsorbed on silica but the structural arrangement of CTAB aggregates on silica in each region should also be taken into account. Obviously, the increased amount of acetophenone adsolubilized into adsorbed CTAB on silica is not directly proportional to the increase in the amount of CTAB adsorbed on silica. Especially, for low and medium surfactant adsorption (regions I and II), the arrangement of CTAB on silica appears to have a greater effect on the adsolubilization of acetophenone than the amount of adsorbed CTAB. In contrast, when approaching high surfactant adsorption (region III), the adsolubilization of acetophenone seems to depend mainly on the amount of adsorbed CTAB on silica.

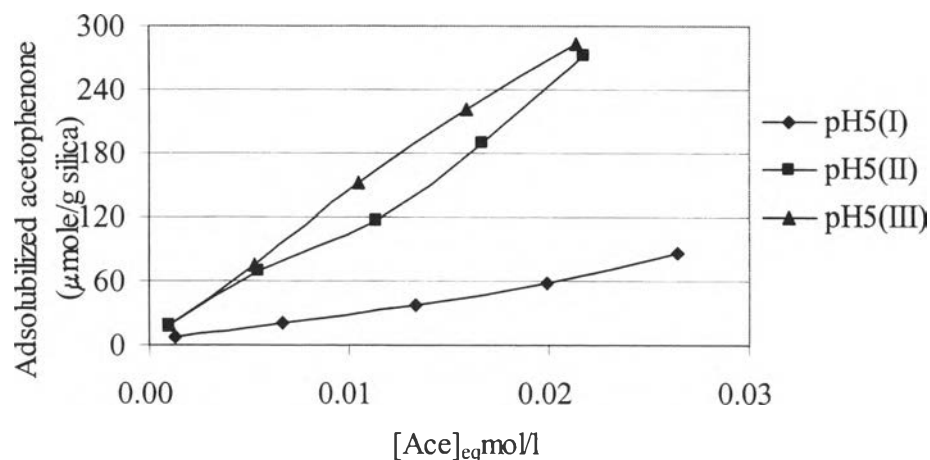


Figure 4.7 Adsorbilization of acetophenone in region I, II, III at pH 5 and $I = 10$ mM.

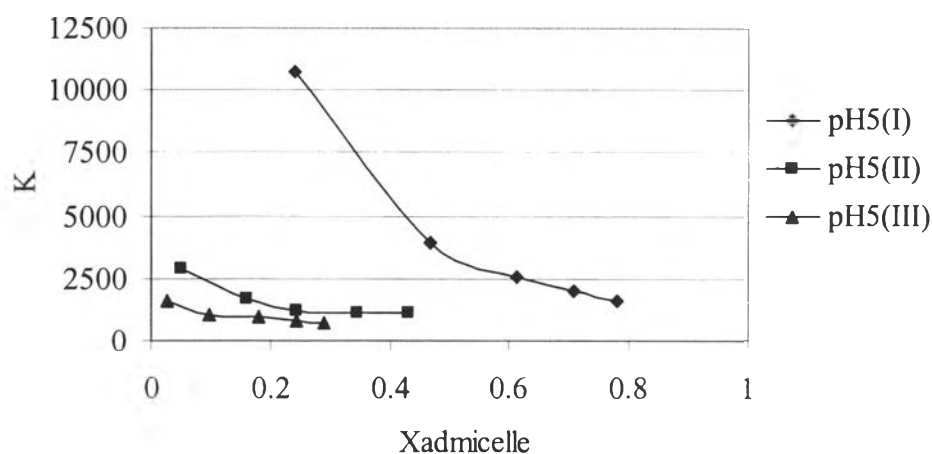


Figure 4.8 The partition coefficient (K) of acetophenone in region I, II, III at pH 5 and $I = 10$ mM.

The plot between the partition coefficient (K) and the mole fraction of acetophenone in the admicelle ($X_{\text{admicelle}}$) is shown in Figure 4.8. It can be seen that the partition coefficient dramatically decreases in the low $X_{\text{admicelle}}$ range and then become quite constant when approaching high $X_{\text{admicelle}}$ range. The partition coefficient decrease with increasing $X_{\text{admicelle}}$ in the range studied (0 to 0.8). The results shown here exhibit a similar trend as observed in our previous study

(Pradubmook, 2000). In contrast to the case of toluene adsolubilization, acetophenone is a highly polar organic solute and thus it is expected that it adsolubilizes primarily into the head group and palisade regions of the admicelle (Rouse *et al.*, 1995). However, the results from the partition coefficient (Figure 4.8) reveal that the adsorbed CTAB on silica surface at higher the amount of CTAB has lower adsolubilization capacity for acetophenone with the same reason described previously (Figure 4.3).

Figure 4.9 shows the plot of acetophenone adsolubilization versus the bulk equilibrium concentration of acetophenone for all three regions at pH 8. The results are very similar to those obtained at pH 5. The adsolubilization of acetophenone increases with increasing acetophenone equilibrium concentration. When compared at different CTAB adsorption, acetophenone adsolubilization at region III is higher than those at region II and I, respectively, which is probably due to the amount of CTAB adsorbed. Figure 4.10 shows the partition coefficient as a function of mole fraction of acetophenone in the admicelle. The partition coefficient of acetophenone adsolubilization is higher at lower the amount of CTAB adsorbed as observed in the adsolubilization at pH 5.

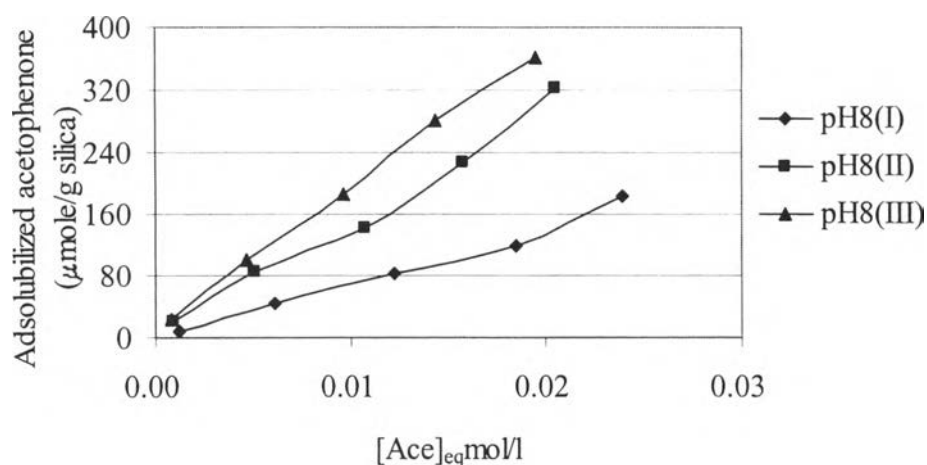


Figure 4.9 Adsolubilization of acetophenone in region I, II, III at pH 8 and I = 10 mM.

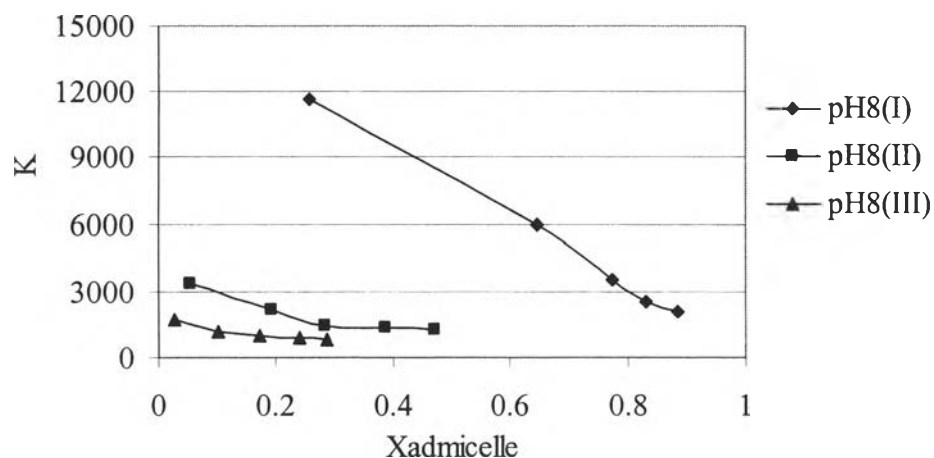


Figure 4.10 The partition coefficient (K) of acetophenone in region I, II, III at pH 8 and I = 10 mM.

Figure 4.11 shows the comparison of acetophenone adsolubilization at two different pH values (5 and 8) in three regions (I, II and III). It should be noted that although the adsorption carried out at different pH, but in the same region (e.g., region I: pH 5 versus 8) yielded relatively the same amount of CTAB adsorbed as shown in Table 4-1A and Table 4-1B. The result in region I can be confirmed that the structural arrangement of CTAB on silica appears to have strongly effect on the adsolubilization of acetophenone than the amount of CTAB adsorbed especially at the low amount of CTAB adsorbed because the amount of CTAB adsorbed on silica in region I of both pH, from Table 4-1A and Table 4-1B, are nearly the same but the amount of adsolubilized acetophenone into adsorbed CTAB in region I of pH 8 are 2.66 times that of pH 5. Moreover the results in region II and III can proved that the effect of the structural arrangement of CTAB aggregates on silica on the adsolubilization of acetophenone decrease when the amount of adsorbed CTAB increased (From region I, II, and III). From Table 4-1A and 4-1B, the amount of CTAB adsorbed on silica in region II and III of pH 8 are 1.014 and 1.064 times that of region II and III of pH 5 whereas Fig. 4.11 shows the amount of adsolubilized acetophenone in region II and III of pH 8 are 1.14 and 1.33 times that of region II and III at pH 5

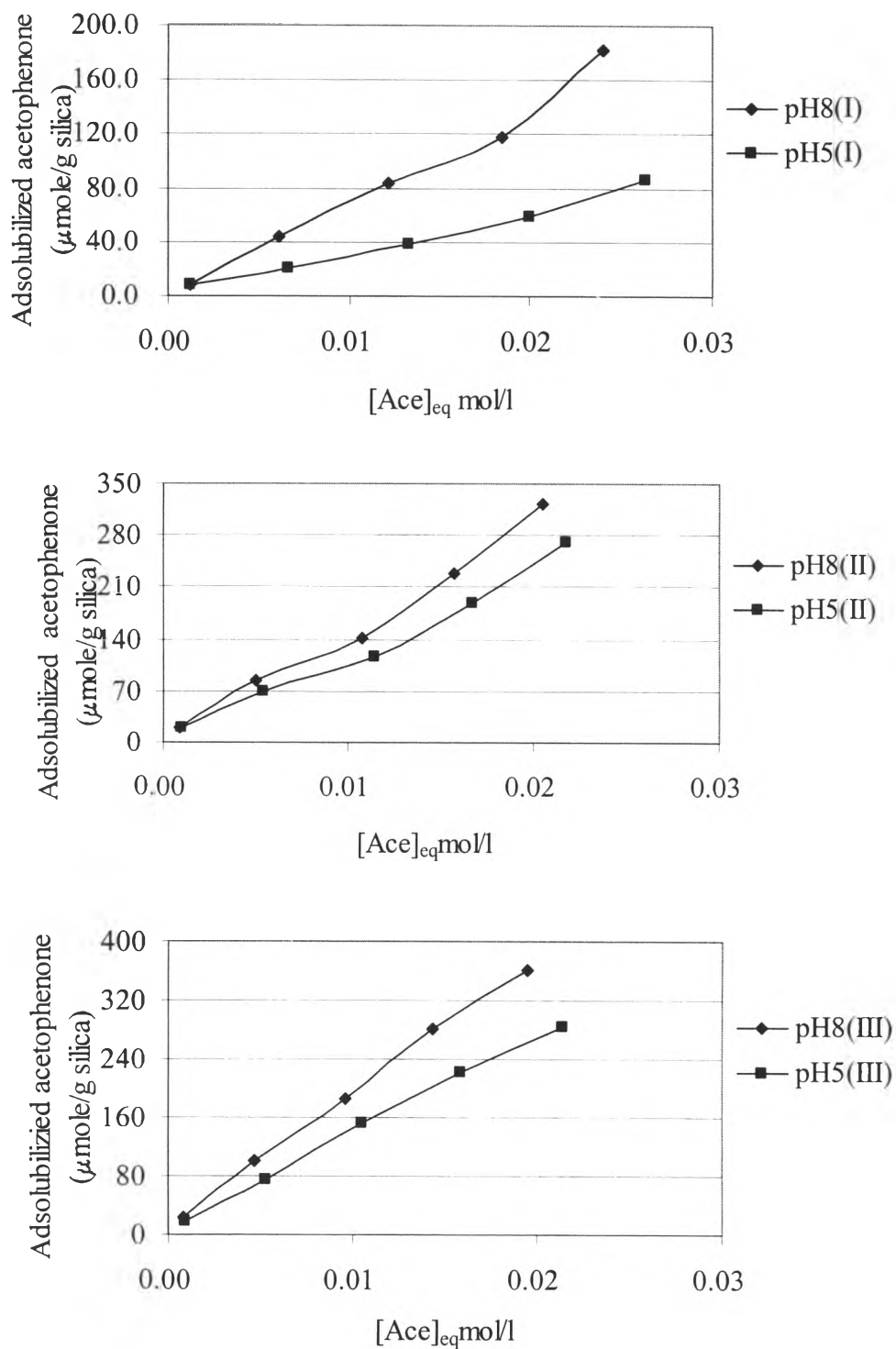


Figure 4.11 Adsolubilization of acetophenone in region I, II, III at pH 5 and 8 and $I = 10 \text{ mM}$

4.2.2 Mixed- Solute Systems

4.2.2.1 Adsolubilization of toluene in the presence of acetophenone

Figures 4.12 and 4.13 show the comparison of adsolubilization of toluene in the presence of acetophenone with toluene adsolubilization in the single-solute system for all three regions (I, II and III) at pH 5 and 8, respectively. In this system, the concentration of toluene studied was varied from 0.7 to 5.5 mmol/l while the concentration of acetophenone was fixed at 0.714 mmol/l. It can be seen that toluene adsolubilization in the presence of acetophenone (mixed-solute system) is almost the same with the single solute system except at region III of pH 8 the adsolubilization of toluene in the presence acetophenone is slightly higher than the toluene adsolubilization in the single-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.

4.2.2.2 Adsolubilization of acetophenone in the presence of toluene

Figures 4.14 and 4.15 show the comparison of adsolubilization of acetophenone in the presence of toluene with acetophenone adsolubilization in the single-solute system for all three regions (I, II and III) at pH 5 and 8, respectively. In this system, the concentration of acetophenone studied was varied from 1.43 to 28.6 mmol/l while the concentration of toluene was fixed at 0.785 mmol/l. It can be seen that acetophenone adsolubilization in the presence of toluene (mixed-solute system) is higher than the acetophenone adsolubilization in the single-solute system at all of three region of each pH. For example, in region II at pH 5 the amount of adsolubilized acetophenone in the presence of toluene is approximately 1.77 times that of the pure acetophenone system. At region II of pH 8 the amount of adsolubilized acetophenone is approximately 2.03 times that of the pure acetophenone system. This synergetic effect has also been observed in the previous studies (Pradubmook, 2000 and Kanjanakhunthakul, 2001). A possible explanation is that toluene in the core swells the bilayer loosening the molecules in the palisade layer, thus providing more volume for acetophenone to adsolubilize. Additionally, the hydrophobic interaction between both adsolubilizates may also

result in higher acetophenone adsolubilization in the presence of toluene (co-solute effect) (Kitiyanan *et al.*, 1996; Kovacs *et al.*, 2002).

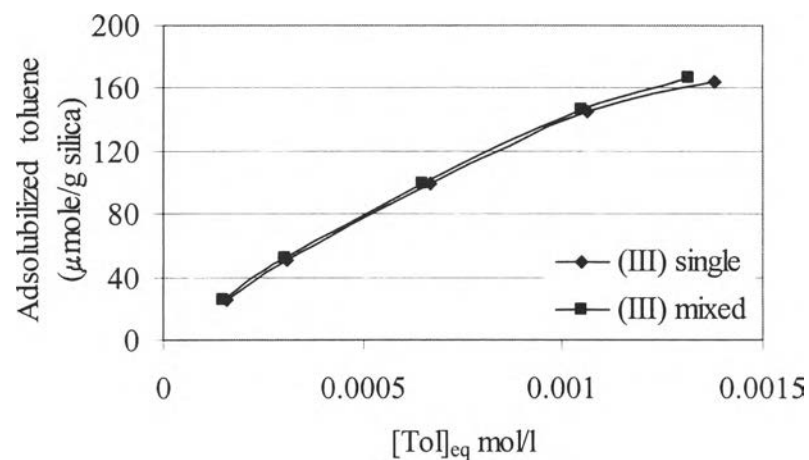
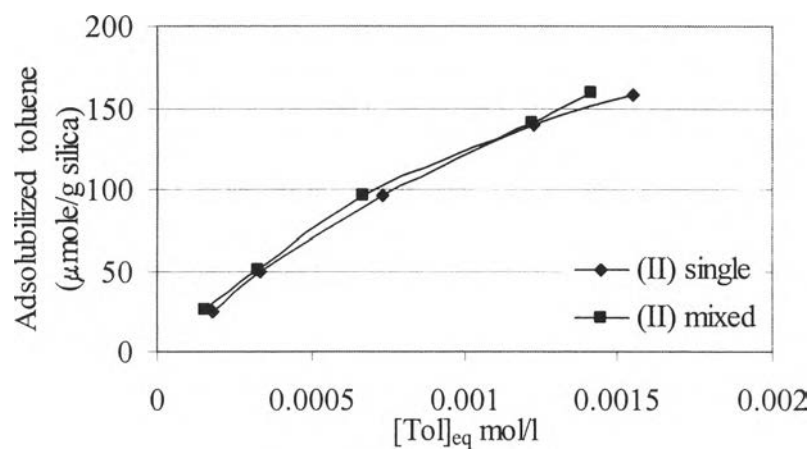
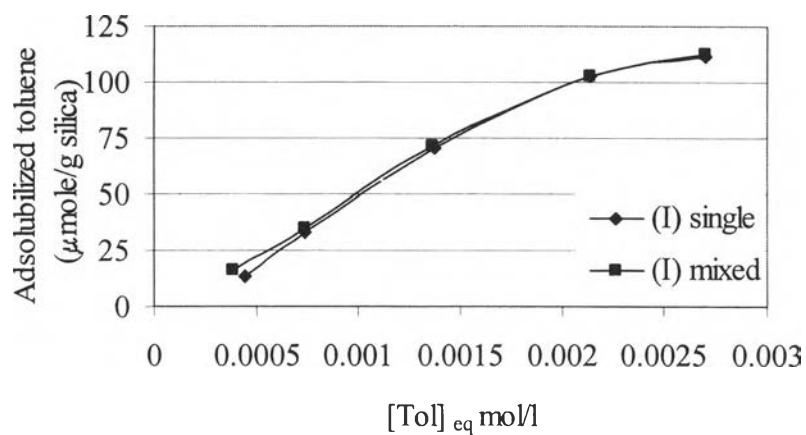


Figure 4.12 Adsolubilization of toluene in the presence of acetophenone in region I, II, III at pH 5 and I=10 mM.

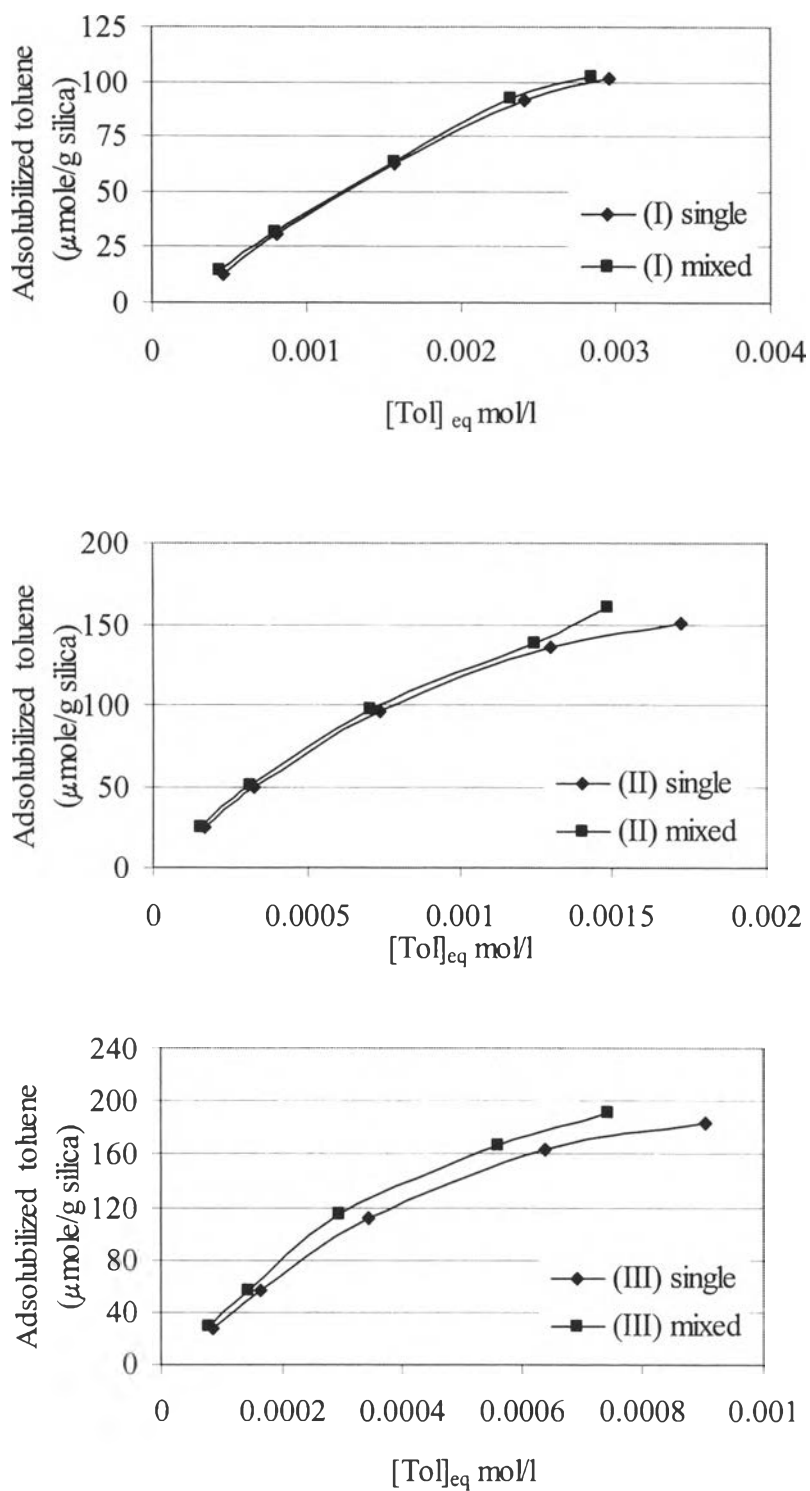


Figure 4.13 Adsolubilization of toluene in the presence of acetophenone in region I, II, III at pH 8 and $I=10$ mM.

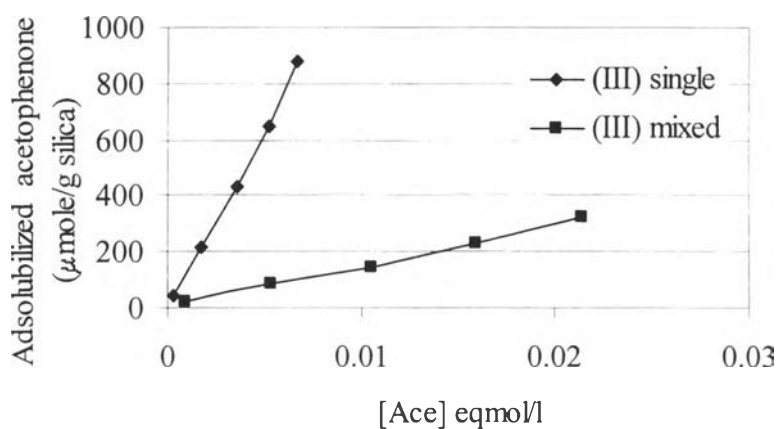
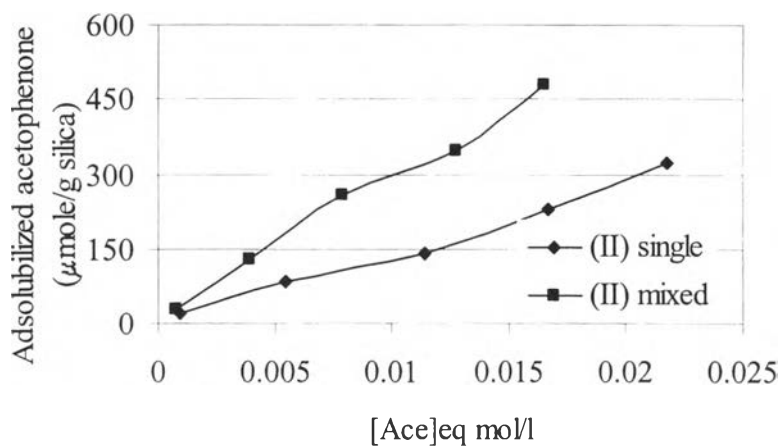
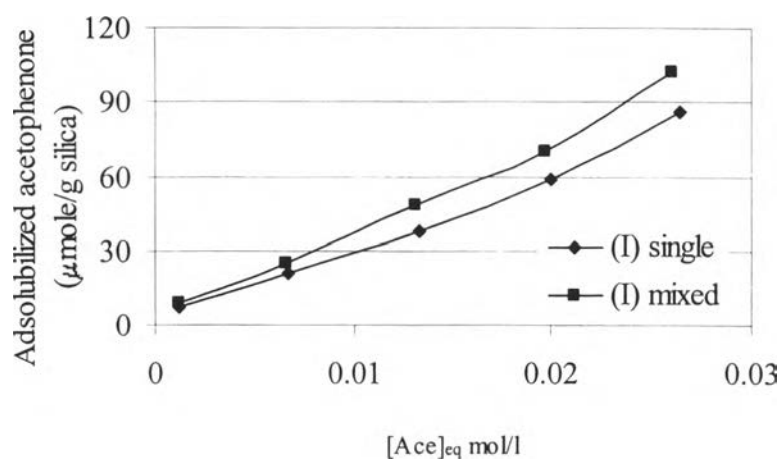


Figure 4.14 Adsolubilization of acetophenone in the presence of toluene in region I, II, III at pH 5 and I=10 mM.

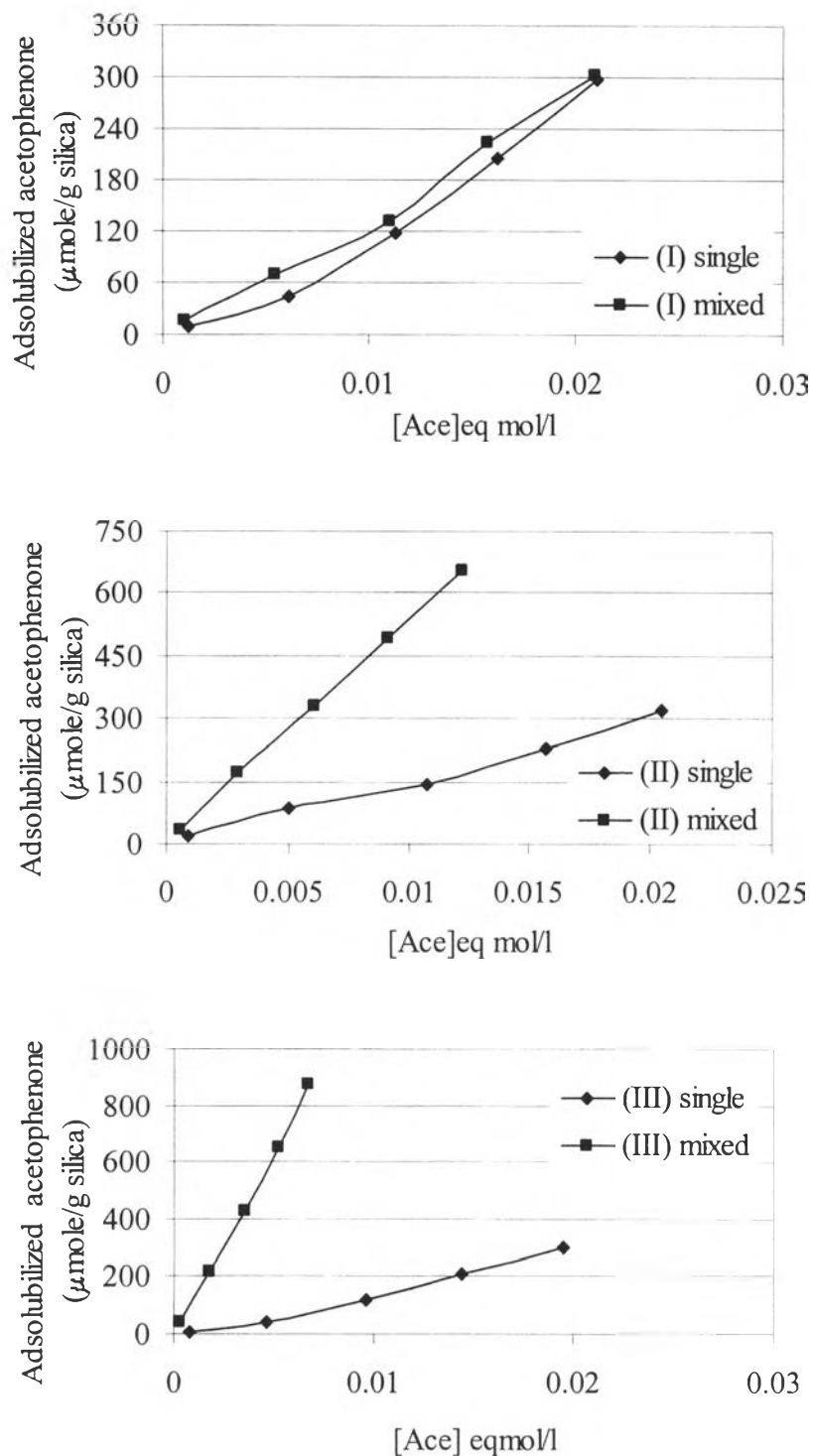


Figure 4.15 Adsolubilization of acetophenone in the presence of toluene in region I, II, III at pH 8 and I=10 mM.