CHAPTER IV

RESULTS AND DISCUSSION

4.1 CTAB Adsorption on Hi-Sil 255

Figure 4.1 shows the CTAB adsorption isotherms at pH 5 and pH 8, plotted on a log-log scale. Adsorption levels increase with increasing charge density on the silica surface (as the pH increases above 3, the point of zero charge). Both isotherms illustrate the characteristic regions II, III, and IV. For pH = 5, region II occurred at equilibrium concentrations of 100 to 400 μM. For pH 8, region II occurred at equilibrium concentrations 70 to 200 μM.

From this figure we can see that for every equilibrium concentration, CTAB adsorption on Hi-Sil 255 silica at pH 8 was higher than at pH 5. From the plateau region, the maximum CTAB adsorption on silica at pH5 and pH 8 are approximately 500 and 600 $\mu mol/g$, respectively. This was an expected result since the surface of the silica is becoming more negatively charged the farther pH is from the point of zero charge (PZC), that is, a pH of 2-3. Increasing the pH leads to higher amounts of head on adsorbed surfactant on the precipitated silica (Holzheu *et al.*, 2000).
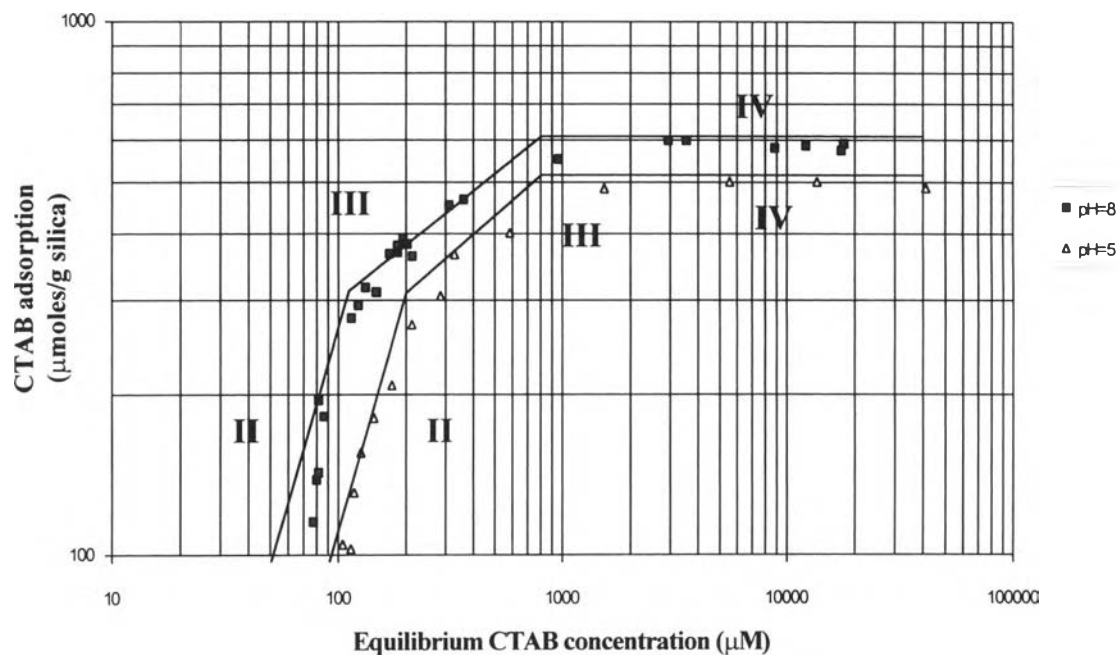
Figure 4.1 Adsorption isotherms of CTAB at pH 5 and 8.

4.2 Adsolubilization Studies

4.2.1 Single-solute systems

4.2.1.1 Adsolubilization of toluene

Figure 4.2 shows toluene adsolubilization versus the bulk equilibrium concentration of toluene at the two pH values (5 and 8). As expected, the adsolubilization of toluene increases with increasing toluene equilibrium concentration. Comparing the adsolubilization of toluene at two different pH values shows that the adsolubilization of toluene at pH 8 is slightly higher than the adsolubilization of toluene at pH 5. The amount of adsolubilized toluene at pH 8 is roughly 1.35 times that at pH 5, due to an increased level of adsorption at pH 8 and an increased core volume due to tighter packing of the admicelle.

This is attributed to the higher plateau adsorption of CTAB on the silica surface at pH 8.   With roughly 20% more adsorbed CTAB at pH 8, we would expect a roughly 20% increase in toluene adsolubilization. Taking a ratio of the equilibrium amount of adsolubilized toluene at pH 8 to that at pH 5 gives us a ratio of approximately 1.35.   This increase over the expected 20% increase could be due to tighter packing of molecules, preventing the penetration of water molecules into the palisade region of the admicelle, effectively increasing the core volume.
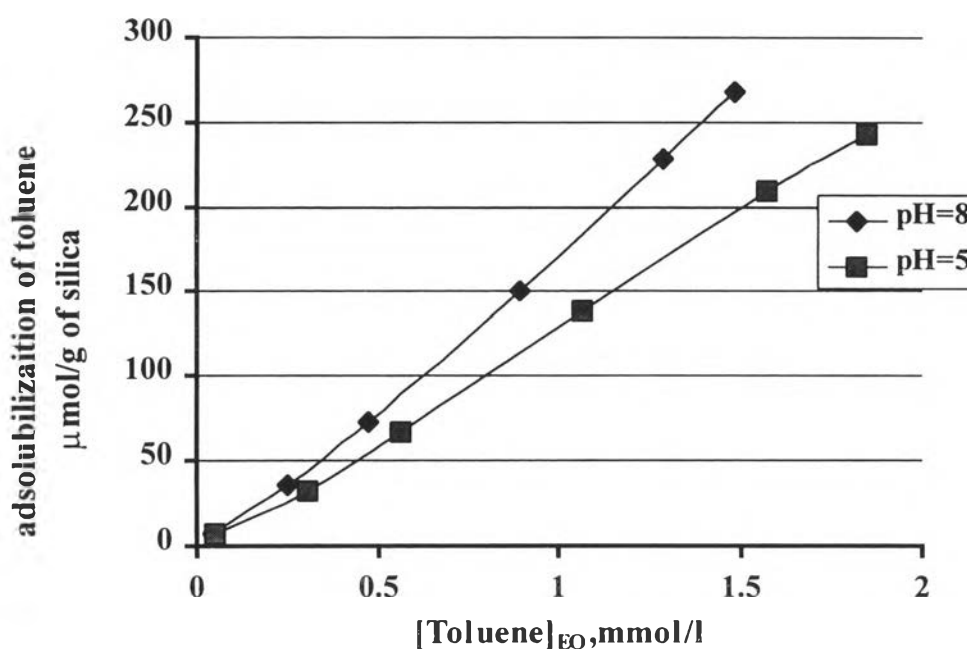

Figure 4.2 Adsolubilization of toluene at pH 8 and 5.

Figure 4.3 is the plot of the adsolubilization equilibrium constant, or partition coefficient, (K) versus the mole faction of toluene in admicelle (X_O). It can be seen that the partition coefficient decreases in the range of $X_O = 0$ to 0.05 and then becomes quite constant in the range of $X_O = 0.05$ to 0.35. Since toluene is a slightly polar organic solute, it is expected that toluene molecules would solubilize into the palisade layer as well as the core of the admicelle.

Thus, according the current theory, K should and does remains constant as the mole fraction of toluene in the admicelle increases (Harwell, 1991). The comparison of the partition coefficient of toluene at pH 5 and pH 8 also reveals that the partition coefficient of toluene at pH 8 is higher than that of toluene at pH 5. The partition coefficient toluene at pH 8 is roughly 1.15 times that at pH 5, due to an increased level of adsorption at pH 8 and an increased core volume due to tighter packing of the admicelle. This could be, as previously discussed, due to tighter packing of molecules effectively increasing the core volume.
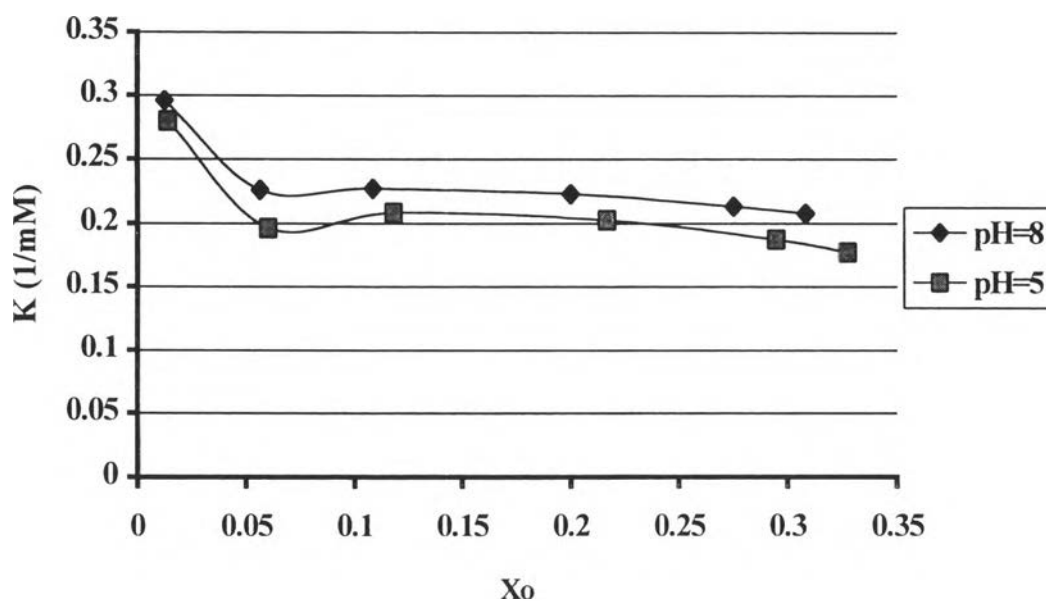

Figure 4.3 Adsolubilization equilibrium constant (K) of toluene at the pH 8and 5.

4.2.1.2 Adsolubilization of Acetophenone

Figure 4.4 shows the plot of acetophenone adsolubilization versus the bulk equilibrium concentration of acetophenone at pH 5 and 8. As expected, the adsolubilization of acetophenone increases with

increasing acetophenone equilibrium concentration in the bulk. From the comparison between the adsolubilization of acetophenone at pH 5 and pH 8, we can see that 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 roughly 2 times that at pH 5, due to an increased level of adsorption at pH 8 due to both the increased adsorption and an increase in the polarity of the admicelle. This behavior is markedly different from the toluene samples. We believe this is due to two factors. First, with a higher level of adsorption, there is more room in the admicelle for adsolubilization. Second, at pH 8 there is a higher polarity to the admicelle, thus causing a higher affinity for acetophenone.
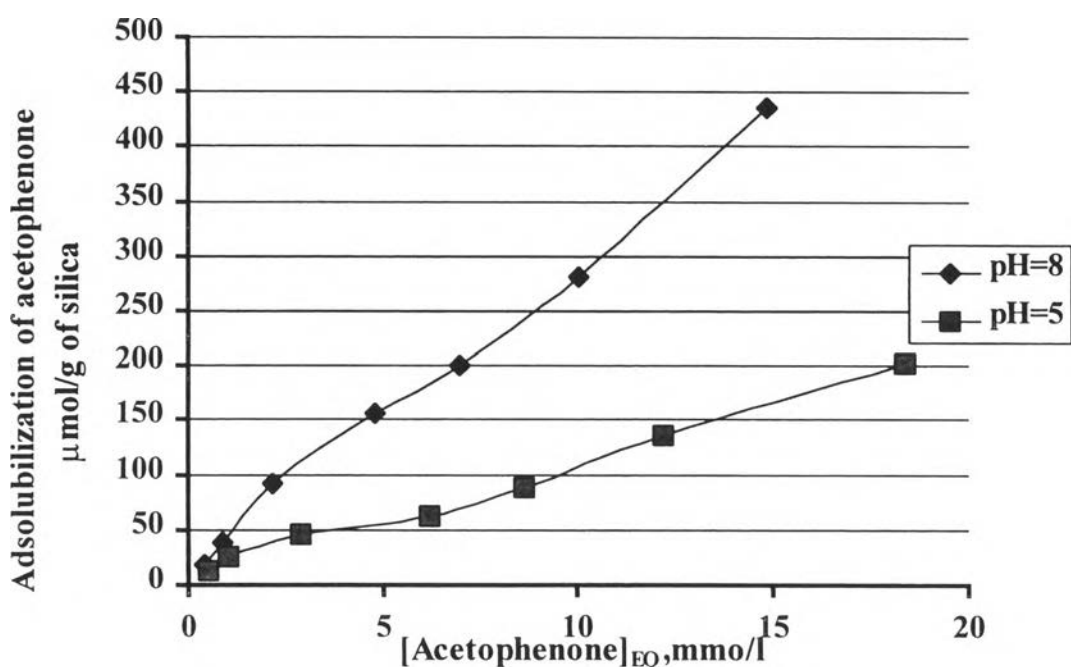

Figure 4.4 Adsolubilization of acetophenone at pH 8 and 5.

The plot between partition coefficient (K) and the mole faction of acetophenone in the admicelle (Xo) is shown in Fig 4.5. As can be seen, the partition coefficient dramatically decreases as the mole fraction of

acetophenone in the admicelle increases. The partition coefficient toluene at pH 8 is roughly 1.4 times that at pH 5, due to an increased level of adsorption at pH 8 and an increased polarity of the admicelle. In contrast to toluene, 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).
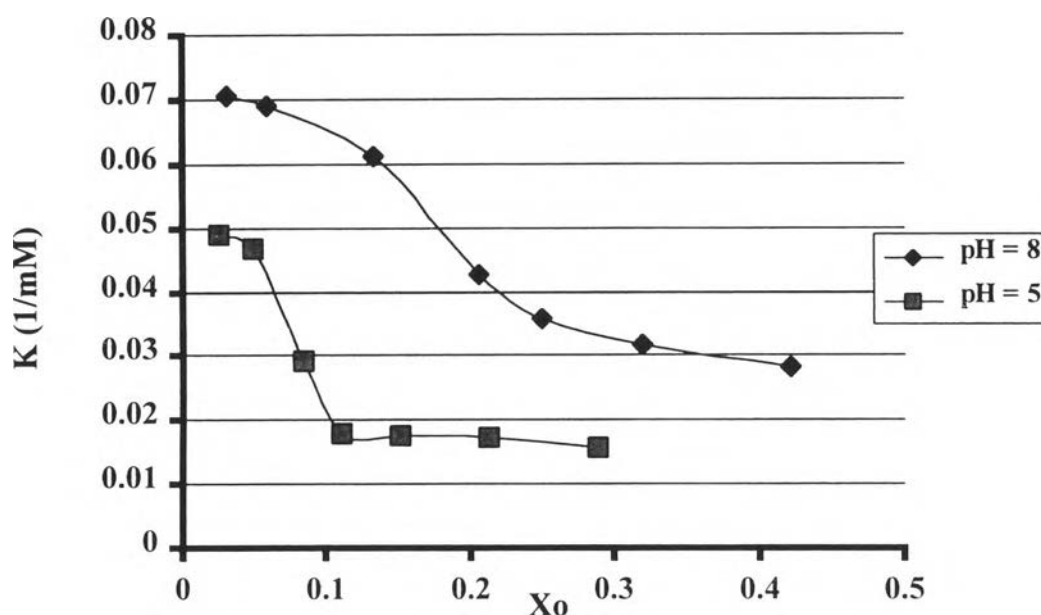

Figure 4.5 Adsolubilization equilibrium constant (K) of acetophenone at the pH 8 and 5.

4.2.2 Mixed-Solute Systems

4.2.2.1 Adsolubilization of Toluene in the Presence of Acetophenone

Figures 4.6 and 4.7 show plot toluene adsolubilization versus equilibrium concentration of toluene in the presence of added acetophenone, at pHs 8 and 5, respectively. The toluene adsolubilization

increases slightly with increasing amounts of acetophenone. At pH 8, the amount of adsolubilized toluene in the presence 1.43 mM and 0.714 mM of acetophenone is roughly 1.5 and 1.25 times that of the pure toluene system. At pH5, The amount of adsolubilized toluene in the presence 1.43 mM and 0.714 mM of acetophenone is roughly 1.33 and 1.13 times that of the pure toluene system, respectively. One possible reason for this is that the presence of acetophenone in the palisade layer displaces water that would normally be in the palisade region, thus effectively increasing the volume of the core. The comparison of adsolubilization of toluene in the co-solute system at pH 8 and pH 5 also reveals the higher co-adsolubilization of toluene at pH 8 than the adsolubilization at pH 5.
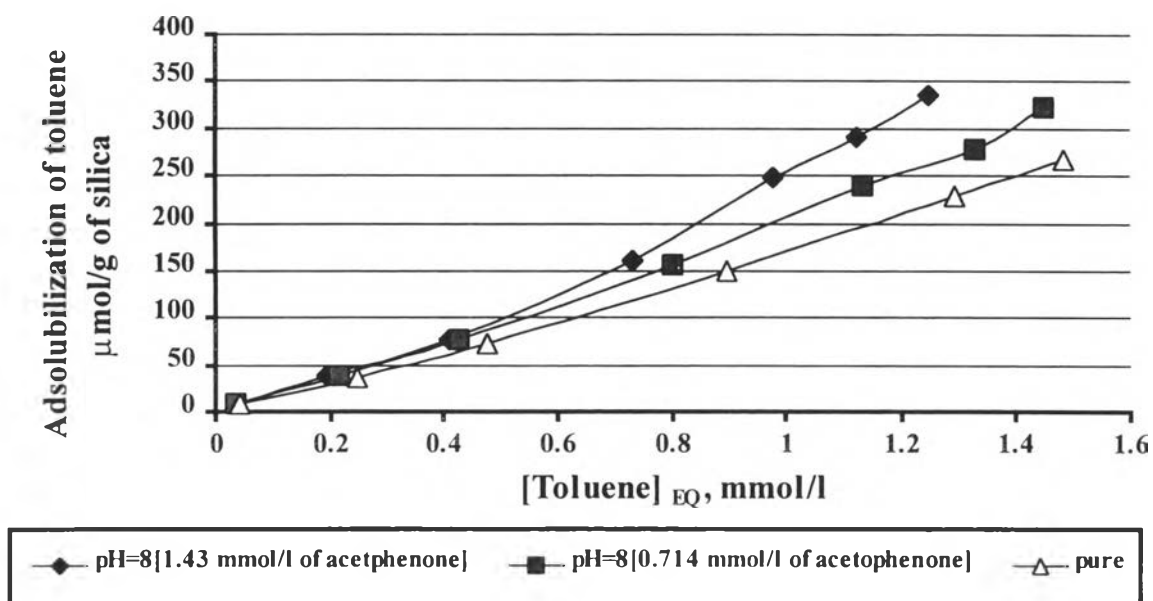

Figure 4.6 Adsolubilization of toluene in the presence of acetophenone at pH 8.
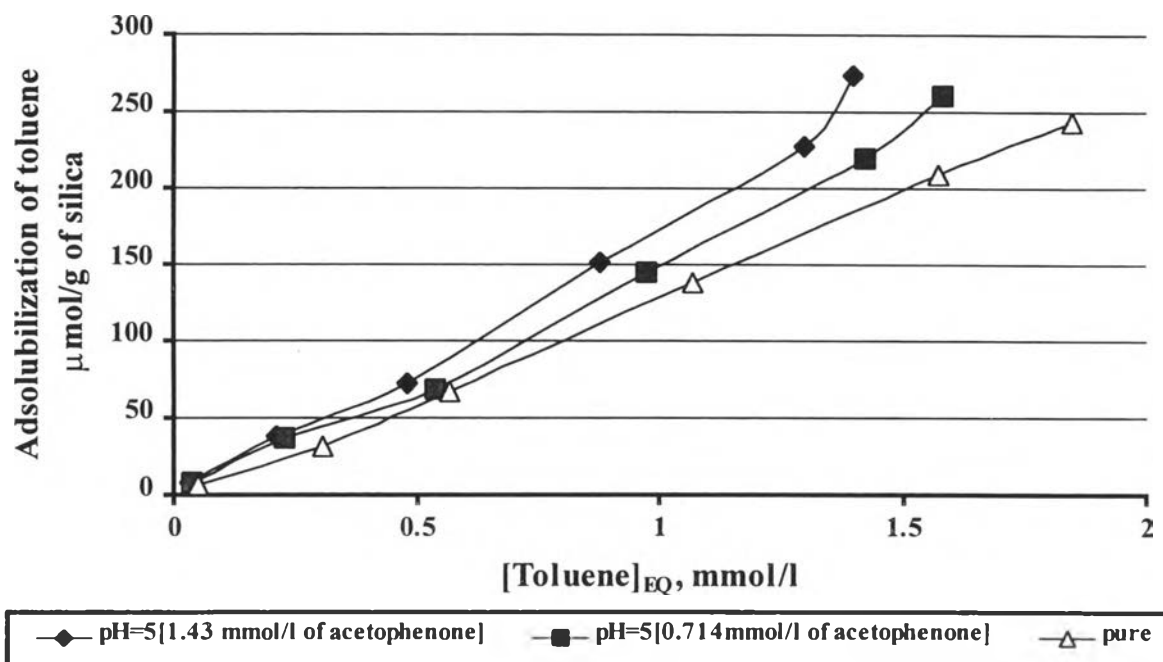
Figure 4.7 Adsolubilization of toluene in the presence of acetophenone at pH 5.

        Figures 4.8 and 4.9 show the partition coefficient (K) versus the mole fraction of toluene in admicelle at pHs 8 and 5. As in the case of toluene alone, the partition coefficient decreases in range of $X_O = 0$ to 0.05 or 0.1 and becomes constant at X_O values above 0.1 mM^{-1}. This behavior is consistent with current theory, since the toluene molecules should adsolubilize into both the palisade layer and the core of the admicelle. The K of toluene in the presence 1.43 mM and 0.714 mM of acetophenone is roughly the same as that of the pure toluene system. The addition of acetophenone does not appreciably change this number because acetophenone can adsolubilize in the palisade layer only.
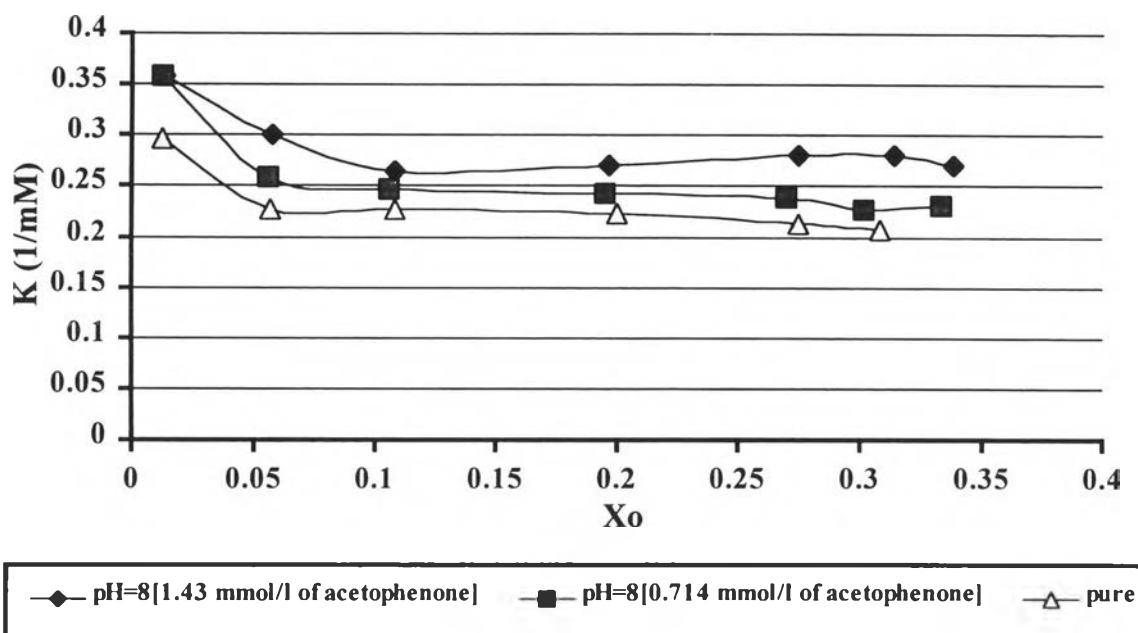
Figure 4.8 Adsolubilization equilibrium constant (K) of toluene in the presence of acetophenone at pH 8.
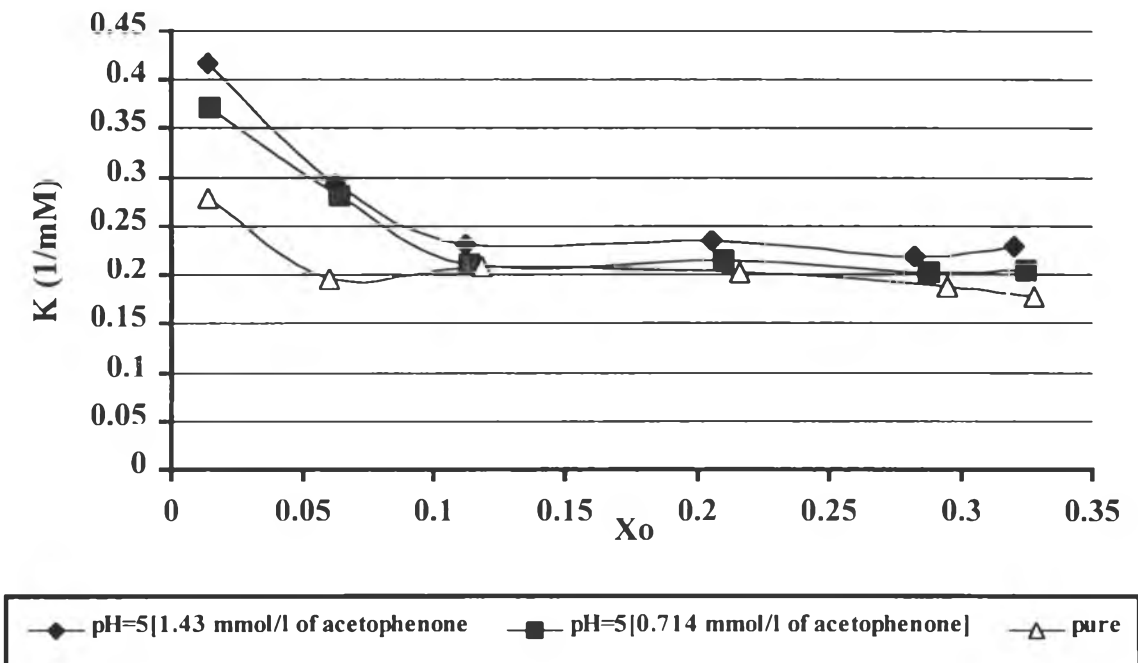

Figure 4.9 Adsolubilization equilibrium constant (K) of toluene in the presence of acetophenone at pH 5.

4.2.2.2 Adsolubilization of Acetophenone in the Presence of Toluene

Figures 4.10 and 4.11 show acetophenone adsolubilization versus the equilibrium concentration of acetophenone in the presence of added toluene at pHs 8 and 5, respectively. In contrast to the previous systems of toluene, the co-solute system shows a much higher acetophenone adsolubilization in the presence of added toluene. At pH 8, the amount of adsolubilized acetophenone in the presence of 1.43 mM and 0.714 mM toluene is roughly 2.85 and 1.75 times that of the pure acetophenone system, respectively. At pH5, the amount of adsolubilized acetophenone in the presence of 1.43 mM and 0.714 mM toluene is roughly 3.33 and 1.33 times that of the pure acetophenone system, respectively. A possible explanation is that toluene molecules in the core swell the bilayer, loosening the molecules in the palisade layer, thus providing more volume for acetophenone to solubilize. Additionally, the hydrophobic interaction between both adsolubilizates may also result in higher adsolubilization of acetophenone into the core. Similar to the single solute system, the adsolubilization of acetophenone in the presence of toluene (co-solute system) at pH 8 is higher than the adsolubilization of acetophenone at pH 5.
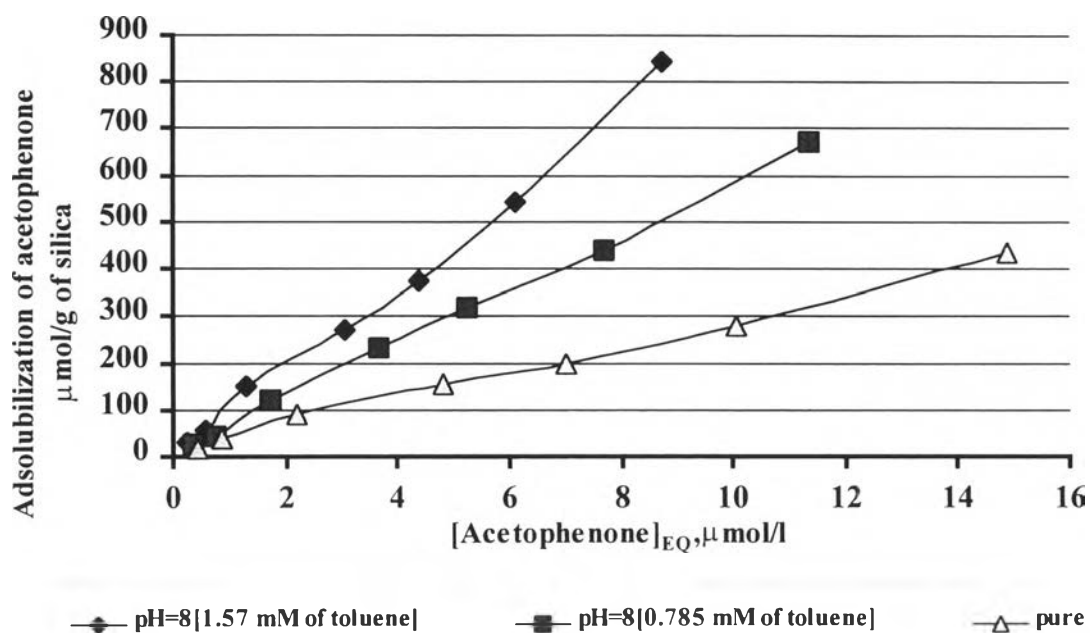
Figure 4.10 Adsolubilization of acetophenone in the presence of toluene at the pH 8.
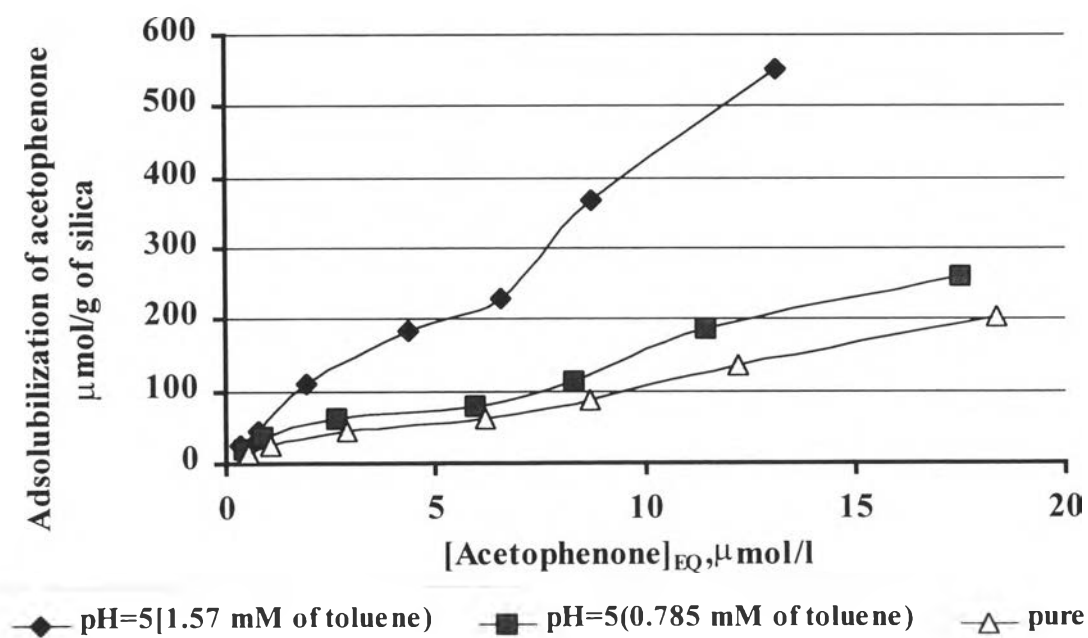

Figure 4.11 Adsolubilization of acetophenone in the presence of toluene at the pH 5.

Figures 4.12 and 4.13 show the partition coefficient (K) versus the mole fraction of acetophenone in admicelle (X_O) for the co-solute systems at pHs 8 and 5, respectively. Similar to the single solute systems (Fig. 4.5), the partition coefficient decreases as the fraction of acetophenone in admicelle increases. Again, as acetophenone partitions primarily into the palisade region, competition for available sites/space increases with increasing levels of adsolubilization. The data also show the higher acetophenone adsolubilization equilibrium constant in the co-solute system than in the pure system (in the absence of toluene). At pH 8, The partition coefficient of acetophenone in the presence of 1.43 mM and 0.714 mM toluene is roughly 2.67 and 2.67 times that of the pure acetophenone system. respectively. At pH5, The partition coefficient of acetophenone in the presence of 1.43 mM and 0.714 mM of toluene is roughly 2 and 5 times that of the pure acetophenone system, respectively. These results comfirm the synergetic effect in the co-solute system as described previously.
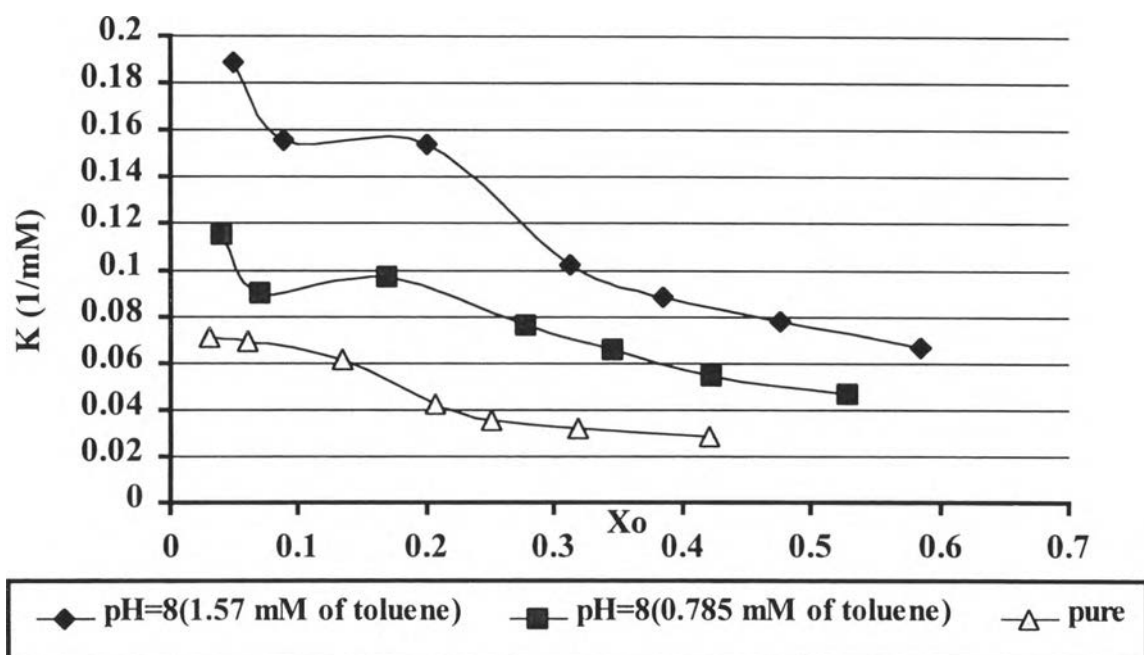
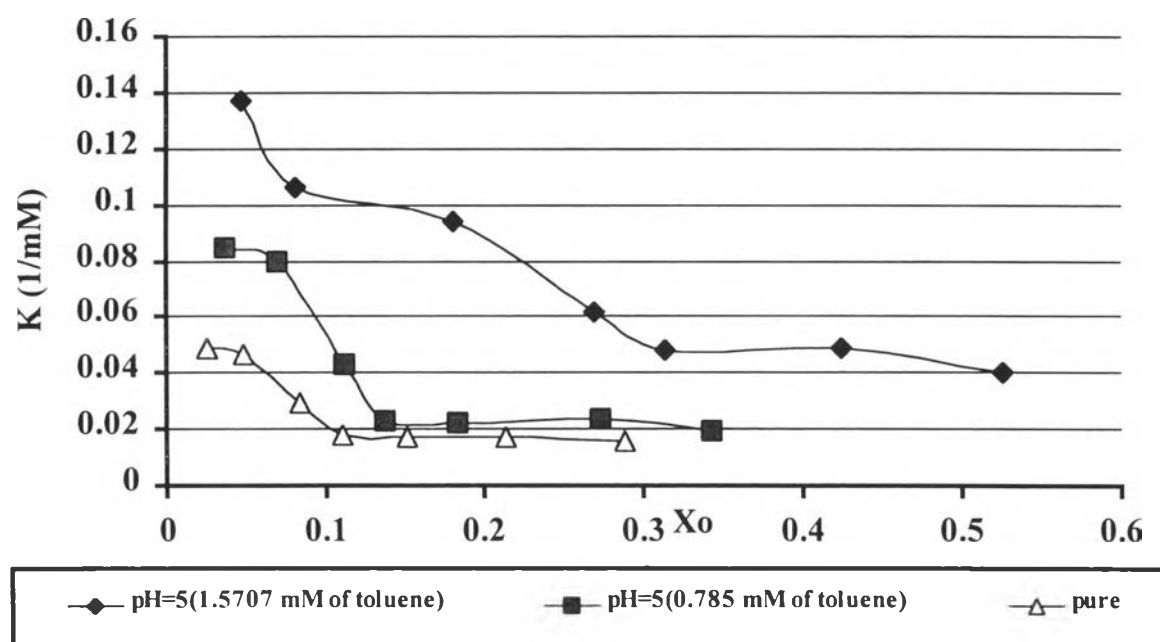**Figure 4.12** Adsolubilization equilibrium constant (K) of acetophenone in the presence toluene pH 8.

Figure 4.13 Adsolubilization equilibrium constant (K) of acetophenone in the presence of toluene at pH 5.