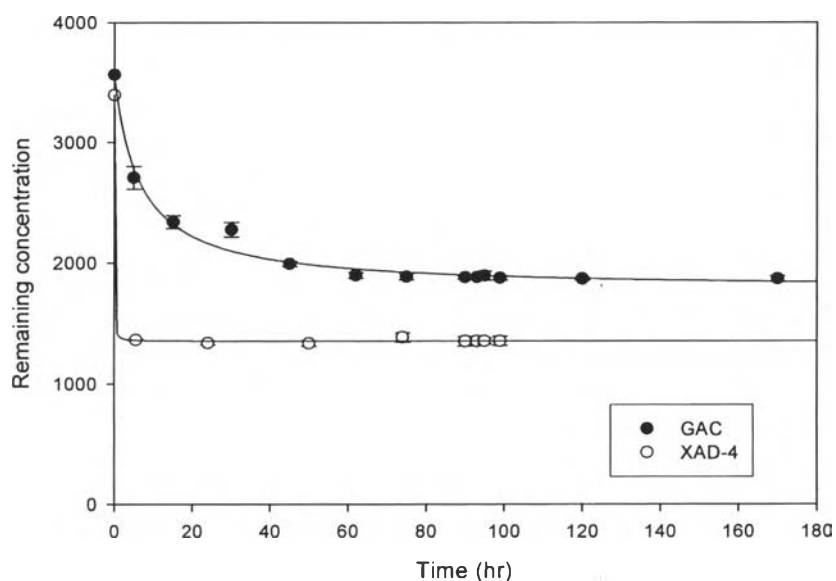


## CHAPTER IV

### RESULTS AND DISCUSSION

Before the adsorption isotherm of surfactant can be constructed, it is imperative to determine the equilibrium time first. The adsorption was carried out and remaining SDS concentration was analyzed at the specific time interval. The remaining concentrations of SDS solution were then plotted as a function of time and from the results equilibrium time could be determined.



**Figure 4.1** Determination equilibrium time of adsorption of SDS at 30°C.

Figure 4.1 shows the remaining concentration of SDS in the solution as a function of time during the adsorption process. For GAC adsorbent, it was found that initially the surfactant adsorption occurred very fast as seen in the figure that the remaining concentration of SDS in the solution decreased rapidly during the first 24 hours, then decreased slowly after that, and became relatively constant after 96 hours. Thus, 96 hours was considered as an equilibrium time of adsorption for GAC adsorbent. While for XAD-4 adsorbent, it was found that the adsorption of SDS occurred very fast during first few hours as the remaining concentration of SDS in the solution decreased rapidly during the first 5-10 hours. After that the

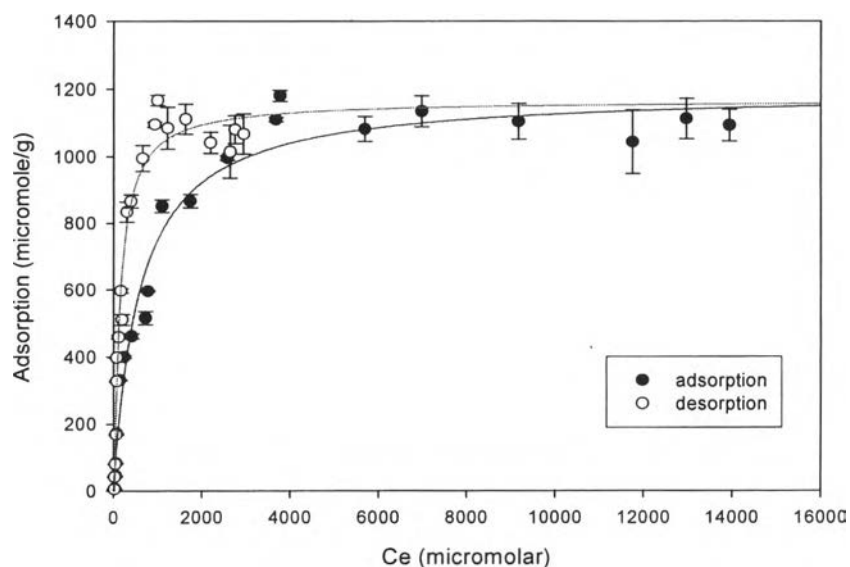
concentration decreased slowly and became relatively constant after 75 hours. Thus, 75 hours was considered as an equilibrium time of adsorption for XAD-4 adsorbent. Since GAC possesses higher surface area than XAD-4 does per weight basis (1,100  $\text{m}^2/\text{g}$  versus 750  $\text{m}^2/\text{g}$ ), GAC can adsorb more SDS than XAD-4, and thus requires more time to reach equilibrium.

After the equilibrium time was determined, the adsorption isotherms were constructed from the equilibrium data by plotting the amount of SDS adsorbed on solid adsorbents and the corresponding equilibrium concentrations. Following the adsorption experiments, the subsequent desorption was performed as described in the previous section. Desorption isotherms were then generated in the same manner as the adsorption isotherms. Adsorption and desorption isotherms were then plotted together on the same graph for comparison as shown in Figures 4.2 and 4.3 for GAC and XAD-4, respectively.

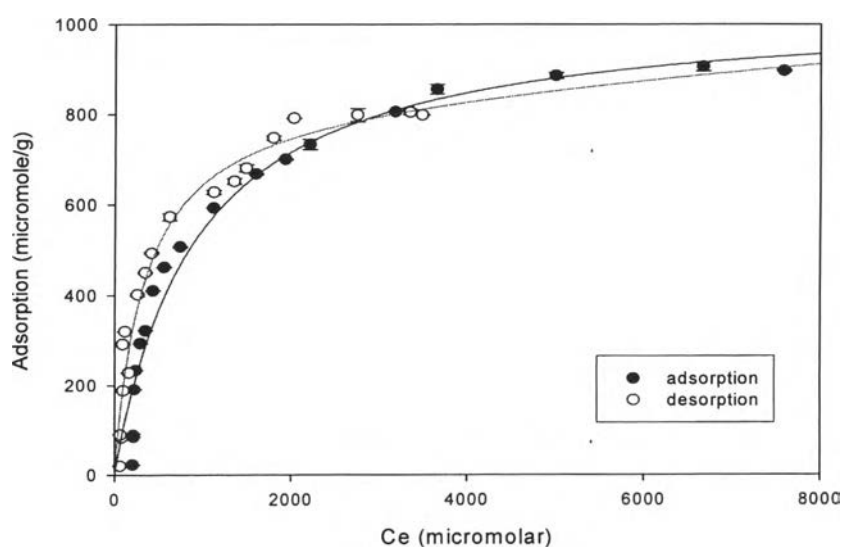
A typical adsorption isotherm was observed in Figure 4.2 in which maximum adsorption of SDS on GAC and critical micelle concentration (CMC) were found to be approximately 1,100 micromole/g adsorbent and 8,200 micromolar, respectively. When comparing the adsorption and desorption isotherms, it is obvious that adsorption of SDS on GAC can not retrace by desorption so that there is a hysteresis between the adsorption and desorption of SDS on GAC. The results observed here clearly reveal that the adsorption of SDS on GAC is not reversible, and thus, it is difficult for SDS to desorb from very hydrophobic surface like GAC.

From Figure 4.3, it can be seen that the maximum adsorbed amount of SDS on XAD-4 was lower than GAC, which was approximately 800-900 micromole/g adsorbent. This is due to the fact that XAD-4 has less surface area available compared to GAC on the same weight basis. For XAD-4, the adsorption and desorption isotherms are very similar as indicated by a very small hysteresis loop. This suggests that adsorbed SDS on XAD-4 can easily desorb from the surface of XAD-4, which is different from the results observed in the desorption of SDS from GAC. This can be explained by two plausible reasons. The first reason concerns the pore size and distribution of the adsorbents. XAD-4 contains larger pore size, are mainly mesopores and macropores whereas more than 75% of pores in GAC are micropores. Therefore, it might much more difficult for SDS to desorb from

micropore. Another reason is that GAC surface is more heterogeneous than XAD-4 since it is derived from natural materials while XAD-4 is a synthetic material. Therefore, GAC surface may contain a variety of functional groups, some of which may interact strongly with SDS.



**Figure 4.2** Adsorption and desorption isotherms of SDS on GAC at 30°C.

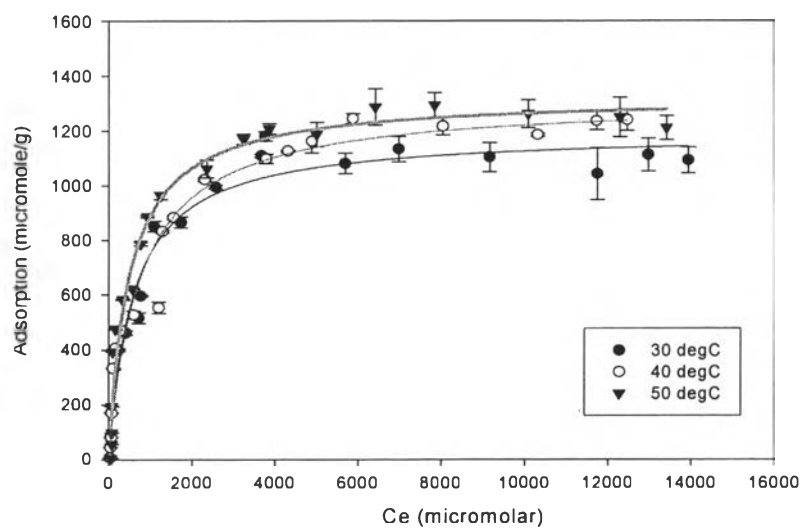


**Figure 4.3** Adsorption and desorption isotherms of SDS on XAD-4 at 30°C.

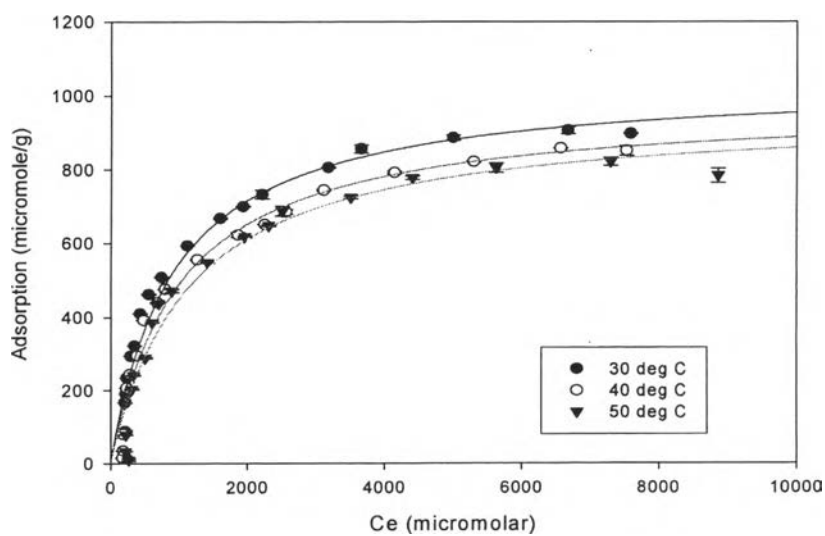
## 4.1 Effect of Temperature on SDS Adsorption/desorption on Hydrophobic Surfaces

### 4.1.1 Surfactant Adsorption

Effect of temperature on the adsorption of SDS on GAC and XAD-4 was studied at three different temperatures, 30°C, 40°C, and 50°C as shown in Figure 4.4 and Figure 4.5.



**Figure 4.4** Adsorption isotherms of SDS on GAC at various temperatures.

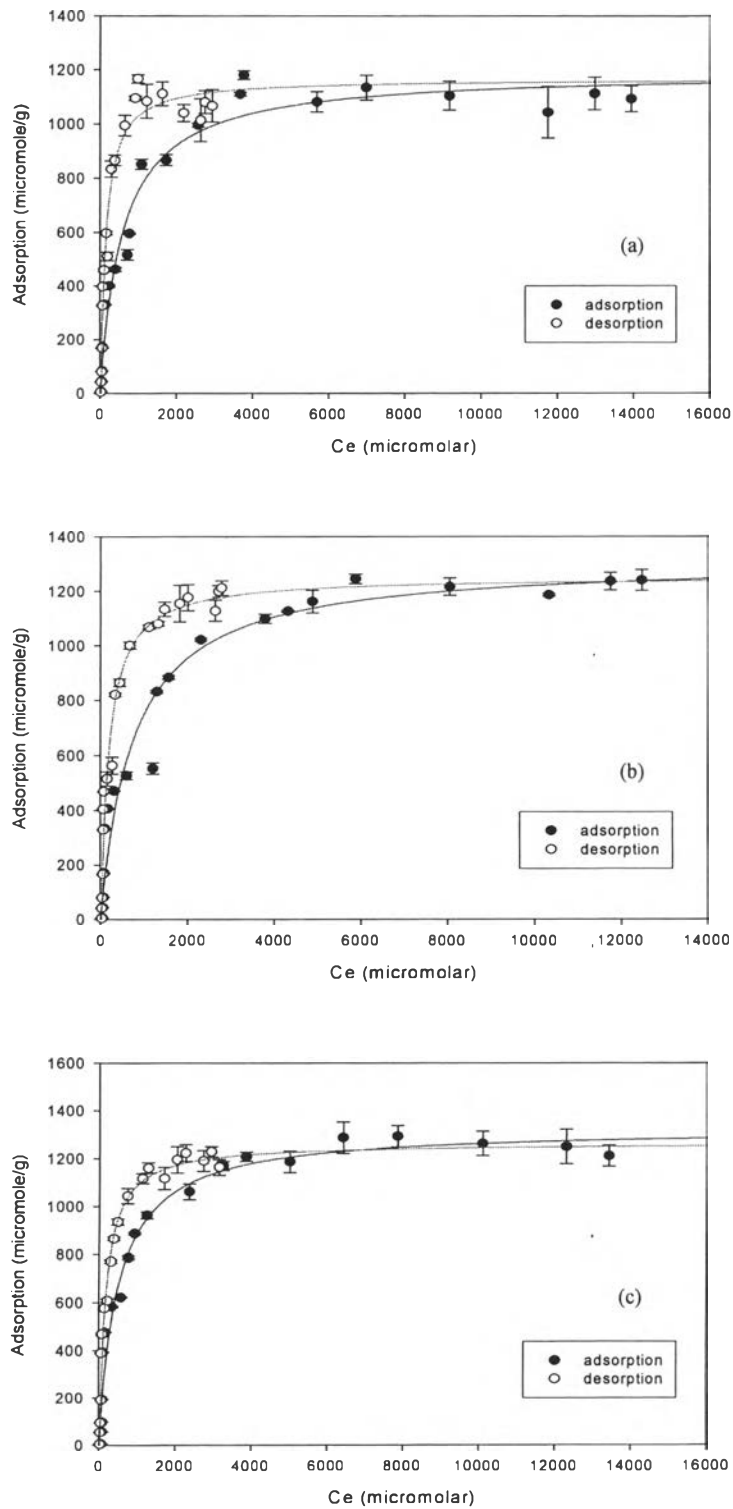


**Figure 4.5** Adsorption isotherms of SDS on XAD-4 at various temperatures.

Figure 4.4 shows the adsorption of SDS on GAC at three different temperatures. The same trend is observed in all temperatures that the adsorption increase with increasing equilibrium surfactant concentration and eventually reached a plateau region at the equilibrium concentration around 8000 micromolar. The adsorption isotherms are very similar and the maximum adsorption for all three temperatures was found to be in a range of 1,100-1,200 micromole/gram. From the results, it can be seen that temperature had little effect on the adsorption of SDS on GAC in the range of temperature studied (30-50°C). Figure 4.5 shows the adsorption of SDS on XAD-4 at three different temperatures. For all three temperatures, a similar trend was observed that the adsorption increased with increasing equilibrium surfactant concentration and eventually reached a plateau region at the equilibrium concentration around 7,000 micromolar. It can be seen that the adsorption of SDS on XAD-4 decreased slightly with increasing temperature, implying the exothermic nature of the adsorption process. However, similar to the SDS adsorption on GAC the effect of temperature on the surfactant adsorption on XAD-4 was not significant in the range of temperature studied.

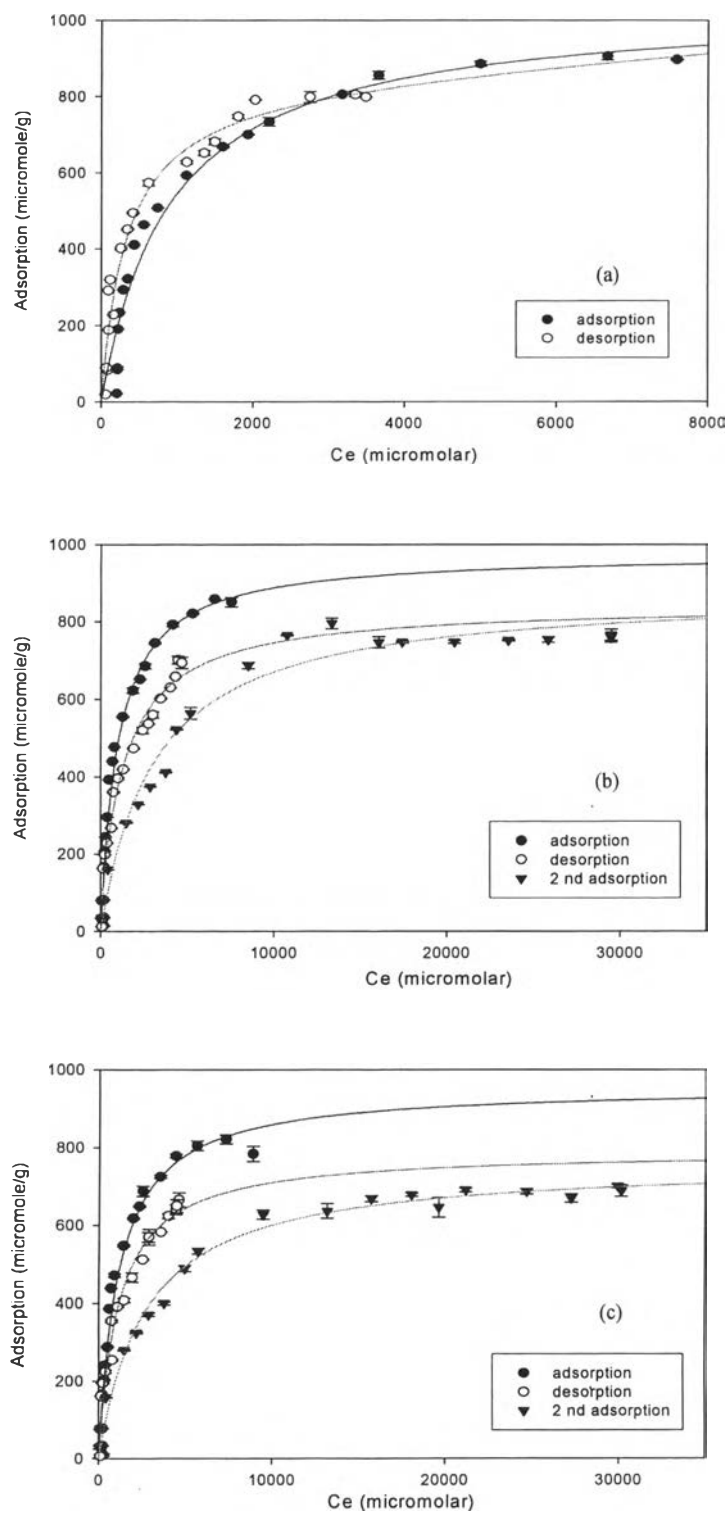
#### 4.1.2 Surfactant Desorption

Following the surfactant adsorption, the surfactant desorption was carried out at the same temperatures (30, 40, 50°C) and then compared with the adsorption results as shown in Figures 4.6 and 4.7. Figures 4.6 (a), 4.6 (b), and 4.6 (c) show the adsorption and desorption of SDS on GAC at 30, 40, and 50°C, respectively. It can be seen from these figures that the desorption curves did not retrace the adsorption curves for all three temperatures, and thus, there was hysteresis existing between the adsorption and desorption isotherms. However, it is important to note that increasing temperature caused a noticeable reduction in the hysteresis loop. At 50°C, very small hysteresis was observed. This can be explained that increasing temperature may cause the weakly adsorbed surfactant molecules on GAC to desorb from the surface. In addition, increasing temperature can also increase the pore diffusion of surfactant molecules being desorbed from the surface.



**Figure 4.6** (a-c) Adsorption and desorption isotherms of SDS on GAC at 30°C, 40°C, and 50°C.

Figures 4.7 (a), 4.7 (b), and 4.7 (c) show the adsorption and desorption of SDS on XAD-4 at 30, 40, and 50°C, respectively. As seen in this figure, even at 30°C the adsorption and desorption curves were not much different as indicated by a very small hysteresis. However, upon increasing temperature from 30°C to 40°C and 50°C, very interesting results were observed that the desorption isotherm was below the adsorption isotherm. The results suggested that the surface of the adsorbent may have changed upon adsorption and desorption at high temperatures (40°C and 50°C). This maybe due to the reorientation or restructuring of surfactant molecules during desorption step or the low thermal stability of XAD-4 itself. Thus, the XAD-4 adsorbent after desorption was subjected to the second adsorption cycle in order to prove this hypothesis. The adsorption isotherms obtained in the second cycle were then plotted on the same graph as seen in Figure 4.7 (b) and Figure 4.7 (c). From the comparison, it is clear that the adsorption in the second cycle after desorption step was much lower than that observed in the first cycle (using fresh XAD-4). The results support that the surfactant adsorption and desorption behavior observed in this part of the study was affected by the change in the configuration of the adsorbed surfactant on the surface of the adsorbent.



**Figure 4.7** (a-c) Adsorption and desorption isotherms of SDS on XAD-4 at 30°C, 40°C, and 50°C.

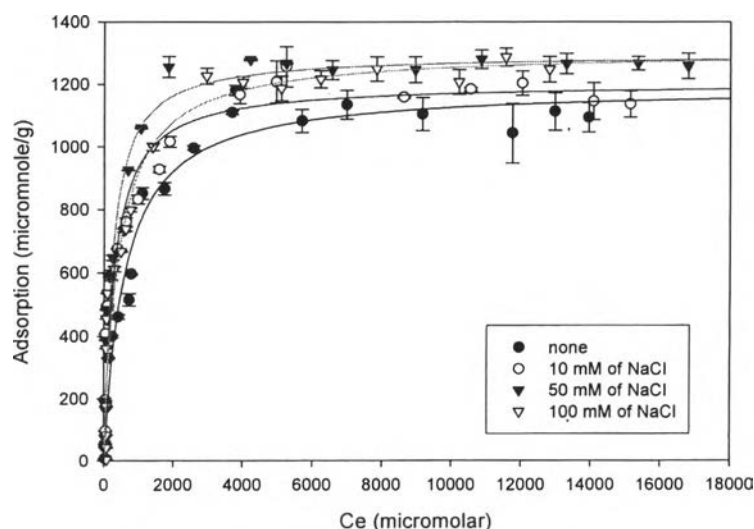


## 4.2 Effect of Salt on SDS Adsorption/desorption on Hydrophobic Surfaces

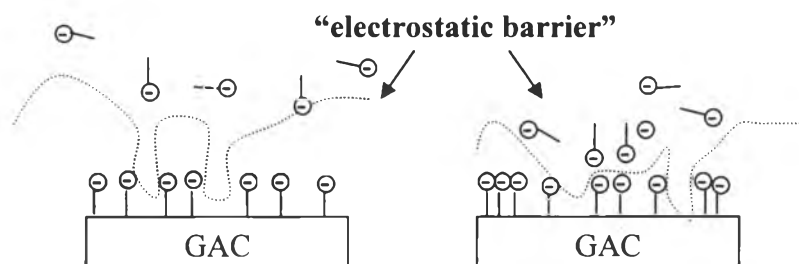
To gain better understanding in the adsorption and desorption of surfactant, effect of salt was studied by using NaCl at various concentrations (10, 50, 100 mM) as shown in Figures 4.8 and 4.10. For this part of the study, temperature was kept at 30°C.

### 4.2.1 Surfactant Adsorption

Figure 4.8 shows the adsorption isotherms of SDS on GAC in the absence and in the presence of NaCl at various concentrations at 30°C. It can be seen that the SDS adsorption onto GAC increased when salt was added into the system and increased with increasing concentration of salt, especially at high salt concentrations (50 and 100 mM). This can be explained that the addition of salt decreased the electrical repulsion between the similarly charged adsorbed ions and incoming ions, thus permitting a closer packing of adsorbed surfactant molecules on the surface as illustrated in Figure 4.9.

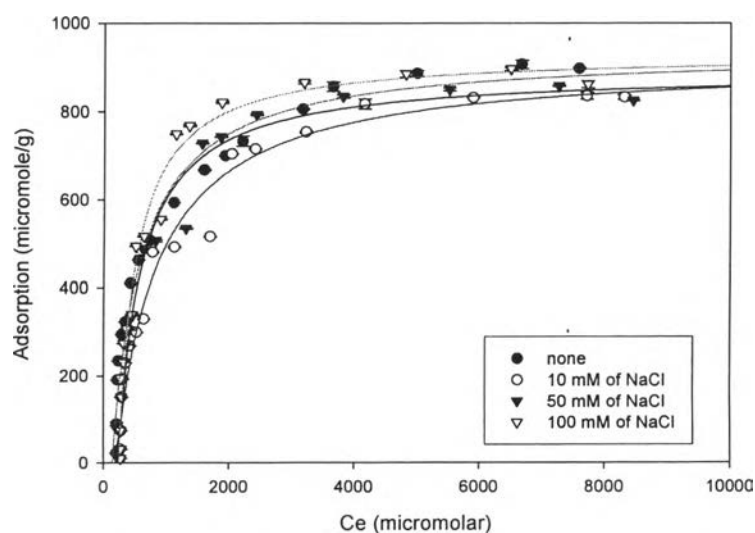


**Figure 4.8** Adsorption isotherms of SDS on GAC at various concentration of NaCl at 30°C.



**Figure 4.9** Sketch of adsorption of SDS on hydrophobic adsorbent: (a) absence of ionic strength, (b) presence of ionic strength. (Stuart *et al.*, 1999).

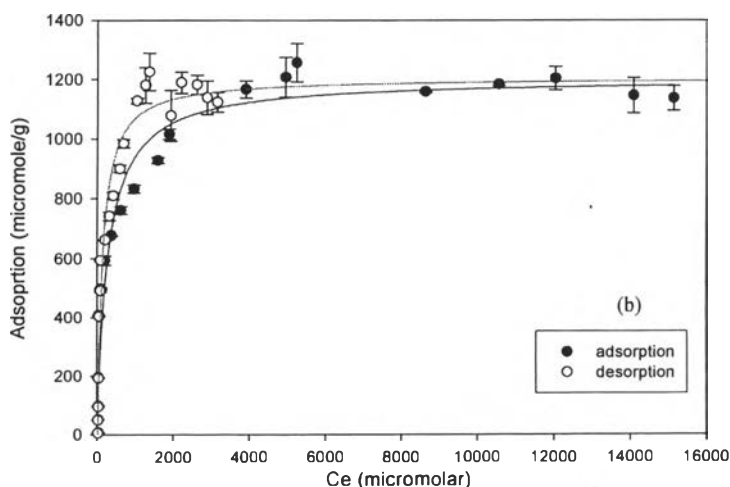
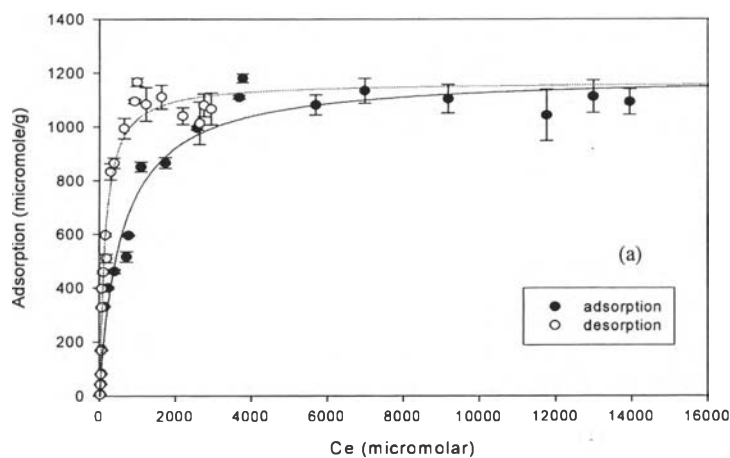
Figure 4.10 shows the adsorption isotherms of SDS on XAD-4 in the absence and in the presence of NaCl at various concentrations at 30°C. It can be seen that the effect of salt on the SDS adsorption on XAD-4 was much less pronounced than that observed in GAC system. The addition of NaCl into the system did not have significant effect on the adsorbed amount of SDS on XAD-4, even at salt concentration as high as 100 mM. The results obtained in this part of the study suggest that the mechanism of the SDS adsorption on GAC and XAD-4 may be different which leads to different desorption behaviors between the two hydrophobic adsorbents as seen in the previous sections.

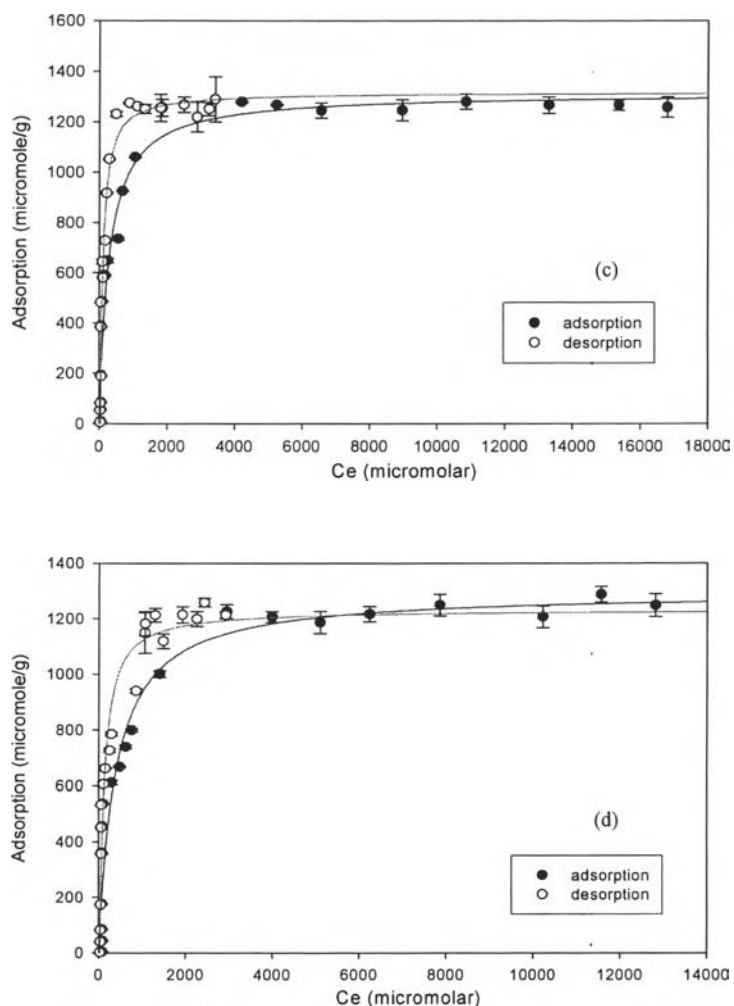


**Figure 4.10** Adsorption isotherms of SDS on XAD-4 at various concentration of NaCl at 30°C.

#### 4.2.2 Surfactant Desorption

Figures 4.11 (a), (b), (c), and (d) show the adsorption and desorption isotherms of SDS on GAC in the absence and in the presence of NaCl at 10, 50, and 100 mM, respectively. It can be seen that the addition of salt into the GAC system not only increased the SDS adsorption on GAC surface but also affect the desorption behavior. The adsorption and desorption isotherms were closer in the presence of salt, resulting in a smaller hysteresis when compared to that observed in the absence of salt. This can be explained in the same manner as described for the effect of salt on the adsorption of SDS on GAC. After adding salt to the system, the adsorbed layer is equilibrated, and thus, the adsorbate can adsorb and desorb reversely.

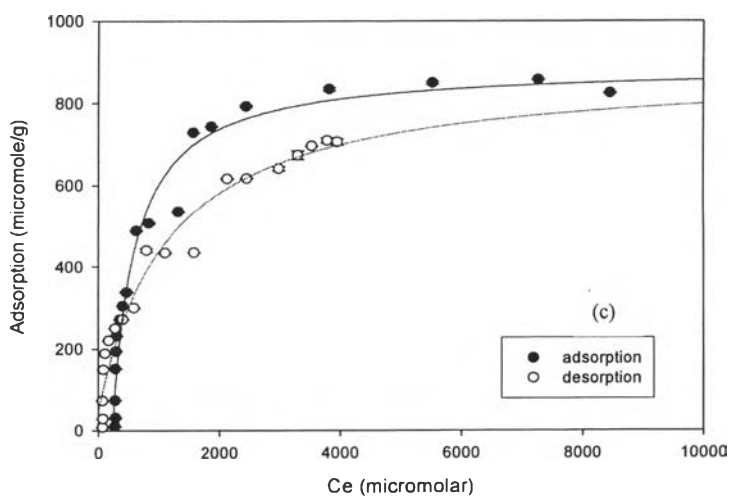
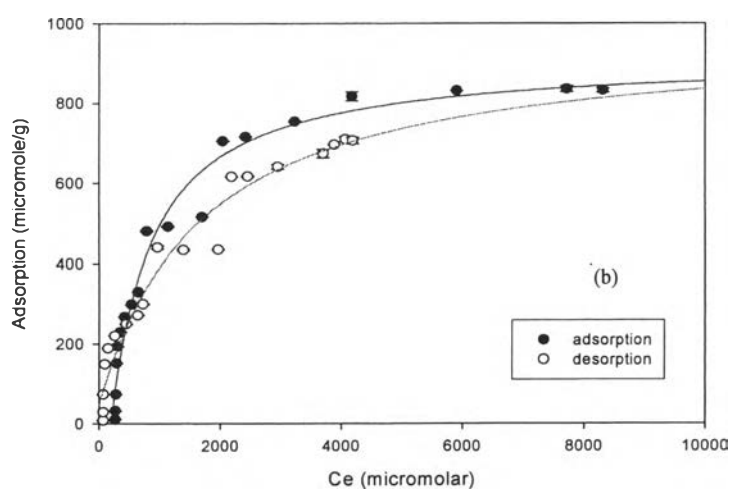
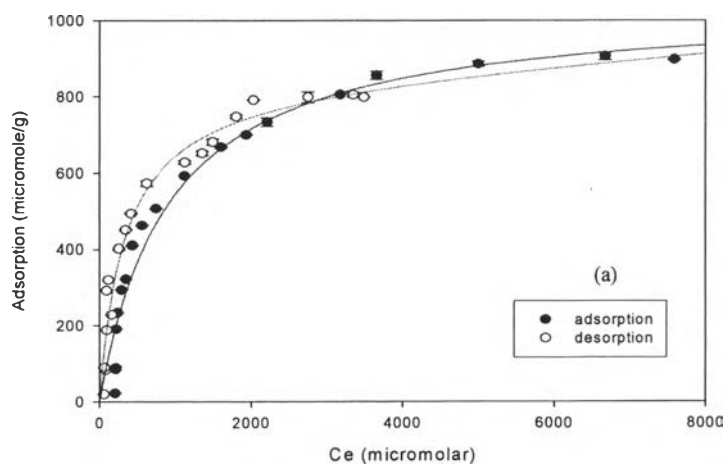


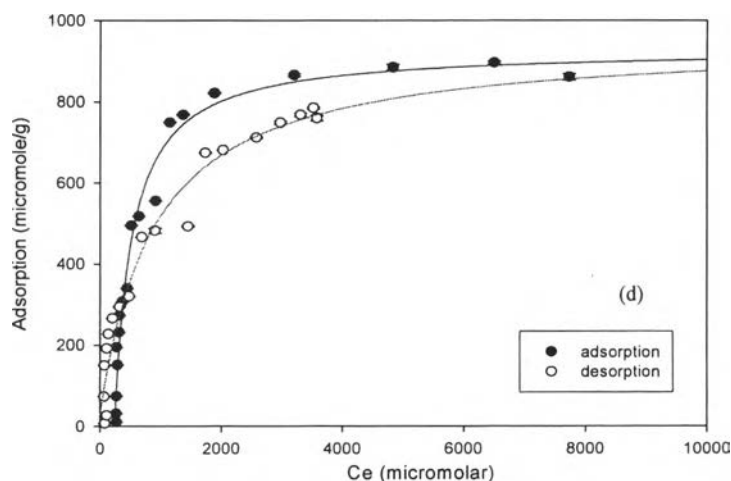


**Figure 4.11** (a-d) Adsorption and desorption isotherms of SDS on GAC in the absence and in the presence of NaCl at 10, 50, and 100 mM.

Figures 4.12 (a), (b), (c), and (d) show the adsorption and desorption isotherms of SDS on XAD-4 in the absence and in the presence of NaCl at 10, 50, and 100 mM, respectively. Similar results as seen in the adsorption of SDS on XAD-4 at different temperatures were observed here that, upon adding salt into the system, the desorption isotherm fell below the adsorption isotherm. This means that some of the desorbed SDS molecules could not re-adsorb on the surface to the same amount originally adsorbed at the same equilibrium concentration. This appearing probably due to possible change of XAD-4 resin surface as described in the previous section.

Another possible reason might be that when salt is added, due to the polar head group of SDS it prefers to stay in aqueous phase more than in solid phase.





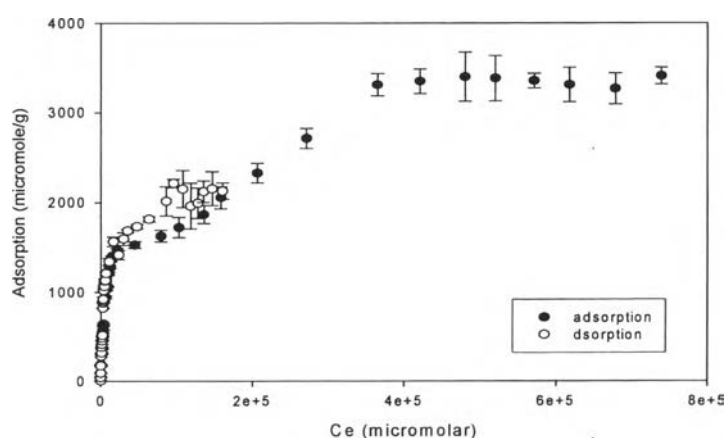
**Figure 4.12** (a-d) Adsorption and desorption isotherms of SDS on XAD-4 in the absence and in the presence of NaCl at 10, 50, and 100 mM.

### 4.3 Structure Effect of Surfactant Sorption to Hydrophobic Surface

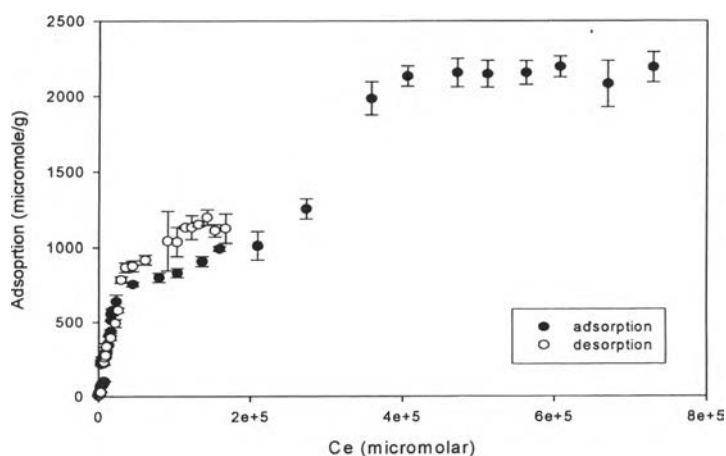
In this part of the study, another anionic surfactant, sodium octanoate, was used in the adsorption and desorption on GAC and XAD-4 for comparison with SDS. Sodium octanoate has  $C_8$  chain which is considerably shorter than SDS ( $C_{12}$ ), and thus, the adsorption and desorption results can aid us in developing better understanding of the effect of hydrophobicity on the sorption of surfactant on this kind of adsorbents. Moreover, head groups of the two surfactants are also slightly different since sodium octanoate has carbonyl group while SDS has sulfate group.

Figures 4.13 and 4.14 show the adsorption and desorption of sodium octanoate on GAC and XAD-4 at 30°C, respectively. A general trend was observed that the adsorption increased with increasing the equilibrium concentration of surfactant and reached the plateau region at a much higher than that observed in case of SDS. The maximum adsorption of sodium octanoate on GAC and XAD-4 were found to be 3,400 and 2,100 micromole/gram, respectively. This is approximately 2-3 times higher than the amount of SDS adsorbed on both surfaces (Figures 4.2 and 4.3). This may be due to the fact that the head group of sodium octanoate which is carboxyl group needs smaller occupied area on the surface than SDS which is sulfate

group (Rosen, 1988; Kilpatrick, 1996). In addition, the hydrocarbon chain length of sodium octanoate which contains only 8 carbon whereas SDS contains 12 carbon, and thus, less repulsion of hydrophobic part can be expected. On the other hand, for the desorption step, hydrophobic interaction seems to be an important role. Hence, sodium octanoate can easily be desorbed from the surface when compared to SDS as it can be seen from the results that the adsorption of sodium octanoate on both adsorbents was much higher than that of SDS.



**Figure 4.13** Adsorption and desorption isotherms of sodium octanoate on GAC at 30°C.



**Figure 4.14** Adsorption and desorption isotherms of sodium octanoate on XAD-4 at 30°C.