CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorption of Sulfur Compounds from Simulated Transportation Fuels

4.1.1 Single-solute Systems

The sulfur compounds used were benzothiophene (BT) and 3-metylthiophene (3MT) for gasoline and dibenzothiophene (DBT) for diesel. Simulated transportation fuels used in this study were isooctane and decane to represent gasoline and diesel, respectively. Thus, the simulated fuels were prepared by mixing benzothiophene or 3-methylthiophene with isooctane to simulate gasoline and mixing dibenzothiophene with decane to simulate diesel.

4.1.1.1 Adsorption of 3-Methylthiophene on NaX and NaY Zeolites

Figure 4.1 shows the adsorption isotherms of 3MT on NaX and NaY zeolites. Y-axis represents the amount of 3MT adsorbed on zeolite and X-axis represents the equilibrium concentration of 3MT in the system. From the results, the adsorption of 3MT increases with increasing equilibrium concentration. Moreover, the adsorption data were found to be well fitted by the Langmuir isotherm. As a result, the maximum adsorption capacity and adsorption equilibrium constant of 3MT on both NaX and NaY zeolites could be obtained from Langmuir equation. The maximum adsorption capacity of NaX and NaY zeolite for 3MT is 1.75 and 1.59 mmole/g, respectively. The adsorption equilibrium constant of NaX and NaY zeolite for 3MT is 0.077 and 0.081 $(\mu mole/g)^{-1}$, respectively. From the isotherms, we can see that at any equilibrium concentration NaX zeolite can adsorb 3MT slightly higher than NaY. In addition, at higher concentration, the difference in the ability to adsorb 3MT is greater. The results suggest that the acidity of the adsorbent is not a prominent factor in 3MT adsorption as NaX has lower acidity than NaY, yet adsorbs more 3MT. This is probably due to higher number of exchangeable sites in NaX than NaY. Moreover, the molecular size of 3MT is relatively small when compared to the zeolite's aperture, and thus more 3MT can be adsorbed at higher concentrations.

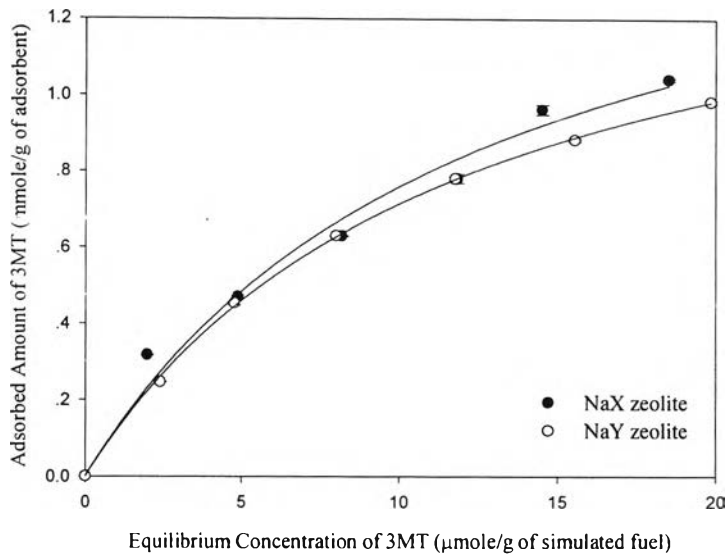

Figure 4.1 Adsorption isotherms of 3-methylthiophene in isooctane on NaX and NaY zeolites at 25°C. Lines are curve-fitting using Langmuir isotherms.

4.1.1.2 Adsorption of Benzothiophene on NaX and NaY Zeolites

Figure 4.2 shows the adsorption isotherms of BT on both NaX and NaY zeolites. Y-axis represents the amount of BT adsorbed on zeolite and X-axis represents the equilibrium concentration of BT in the system. From the results, a general trend can be observed that initially the adsorption of BT increases with increasing equilibrium concentration and then become relatively constant. The adsorption data were found to be well fitted by full Langmuir isotherm as also shown in the figure. As a result, the maximum adsorption capacity and adsorption equilibrium constant of BT on both NaX and NaY zeolites could be obtained from Langmuir equation. The maximum adsorption capacity of NaX and NaY zeolite for BT is 1.34 and 1.17 mmol/g, respectively. The adsorption equilibrium constant of NaX and NaY zeolite for BT is 2.71 and 1.54 $(\mu mole/g)^{-1}$, respectively. The preferentially adsorption observed from both isotherms is primarily due to the presence of benzene ring in the structure of BT which can interact with zeolite acidic surface via π-bonding (Yang *et al.*, 2001). It is also observed that at any equilibrium concentration NaX zeolite can adsorb much higher amount of BT than NaY, even in

the low concentration region. This can be attributed to higher sorption sites in NaX as compared to NaY. This results in higher surface energy of NaX, thus leading to higher interaction with the sulfur compound.

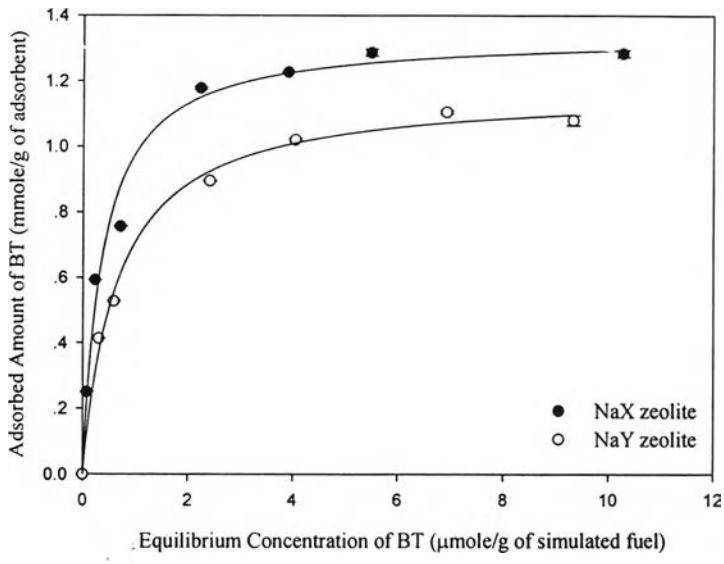

Figure 4.2 Adsorption isotherms of benzothiophene in isooctane on NaX and NaY zeolites at 25°C. Lines are curve-fitting using Langmuir isotherms.

4.1.1.3 Adsorption of Dibenzothiophene on NaX and NaY Zeolites

Figure 4.3 shows the adsorption isotherms of dibenzothiophen on NaX and NaY zeolites. Y-axis represents the amount of DBT adsorbed on zeolite and X-axis represents the equilibrium concentration of DBT in the system. It can be seen that the adsorption of DBT on both zeolites exhibits a Langmuir-type isotherm. The experimental data were fitted with the Langmuir isotherm and the maximum adsorption capacity and adsorption equilibrium constant of DBT on both NaX and NaY zeolites were determined. The maximum adsorption capacity of NaX and NaY zeolite for DBT is 1.09 and 1.11 mmol/g, respectively. The adsorption equilibrium constant of NaX and NaY zeolite for DBT is 5.16 and 3.39 $(\mu mole/g)^{-1}$, respectively. Both adsorption isotherms show a strong or preferential adsorption of DBT on both zeolites. Similar to BT, the slope of DBT isotherms is very steep, much steeper than that of 3MT isotherms. This is attributed to the benzene ring in the structure of DBT,

which can form π-bond with the zeolite surface as discussed previously. This effect should be more significant in case of DBT than in 3MT and BT adsorption since DBT has two benzene finctional groups in its structure. Therefore, DBT has more π-electrons that can be polarized or induced more easily when exposing to acidic surfaces like NaX and NaY. It can also be seen that the adsorption of DBT on both NaX and NaY zeolites are also very similar. This may be due to a combination of the influences from both number of sorption sites and the acidity of both zeolites. NaX has more higher number of sites for solute adsorption but its acidity is lower than NaY. However, the effect of higher acid sites is not much pronounced in this case, especially in high concentration region. This may be the result of steric hindrance effect on the adsorption of relatively big molecule like DBT.

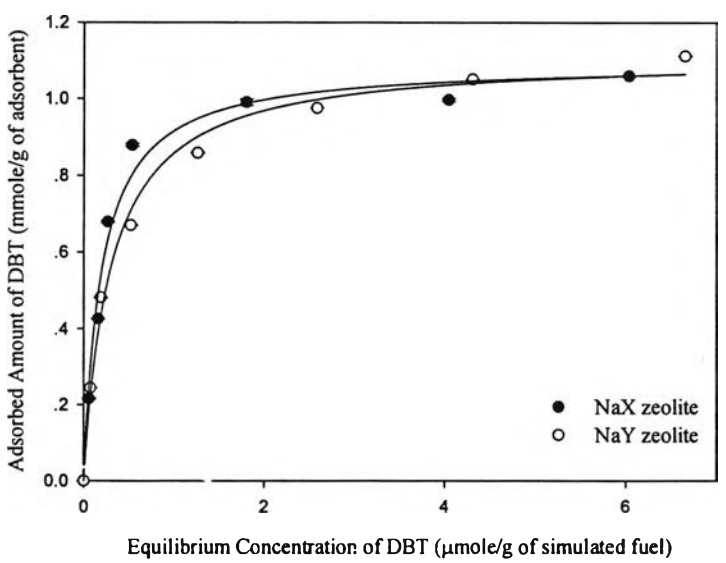

Figure 4.3 Adsorption isotherms of dibenzothiophene in decane on NaX and NaY zeolites at 25°C. Lines are curve-fitting using Langmuir isotherms.

From Figures 4.1 to 4.3, it can be obviously seen that adsorption of BT and DBT are much higher than that of 3MT. Both BT and DBT are better adsorbed by NaX zeolite than 3MT, especially at low concentration. The preferential adsorption observed here suggests that the benzene functional group in BT and DBT structure is an important factor in the adsorption of sulfur compounds on zeolite. In

addition, at low concentration, the zeolites can adsorb DBT slightly higher than BT. It may be a reason of two benzene rings in DBT structure. In contrast, the zeolites can more adsorb BT than DBT in the high concentration region. The steric effect and molecular size may be the reasons.

4.1.2 Mixed-solute System

In this part of the study, the adsorption of mixed sulfur compounds on NaX and NaY zeolites was examined in simulated gasoline system by using isooctane containing both 3MT and BT. Figures 4.4 and 4.5 show the adsorption isotherms of 3MT and BT on NaX and NaY zeolites. Y-axis represents the amount of 3-methylthiophene and BT adsorbed on zeolite and X-axis represents the equilibrium concentration of 3MT and BT in the mixed-solute system. From the results, the adsorption of 3MT and BT increased with increasing equilibrium concentration. Moreover, the adsorption data were found to be well fitted by Langmuir isotherm. As a result, the maximum adsorption capacity and adsorption equilibrium constant of 3MT on both NaX and NaY zeolites could be obtained from Langmuir equation as shown in Table 4.1.

Table 4.1 The maximum adsorption capacity and the adsorption equilibrium constant of 3MT and BT in mixed-solute system on both NaX and NaY zeolites

Adsorbents	Sulfur Compounds	Q_{max} (mmol/g)	K $(mmol/g)^{-1}$
NaX	3-metylthiophene	0.45	0.74
	Benzothiophene	1.21	3.65
NaY	3-metylthiophene	0.42	0.71
	Benzothiophene	1.12	2.83

From the results, it can be obviously seen that the adsorption of BT is much higher than that of 3MT for both NaX and NaY systems. BT is preferentially adsorbed by the zeolites than 3MT, especially at low concentration. The preferential adsorption observed here is attributed to the benzene funtional group in BT which plays an important role in the adsorption of sulfur compounds on zeolite. It has been

known that π-electrons in benzene ring can form bond with adsorption site of zeolite (Hernandez *et al.*, 2003).

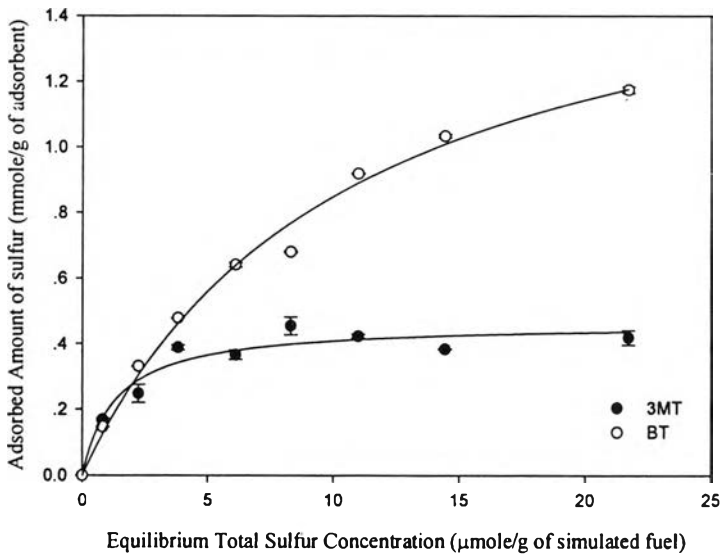

Figure 4.4 Adsorption isotherms of 3MT and BT on NaX zeolite in mixed-solute system at 25°C. Lines are curve-fitting using Langmuir isotherms.

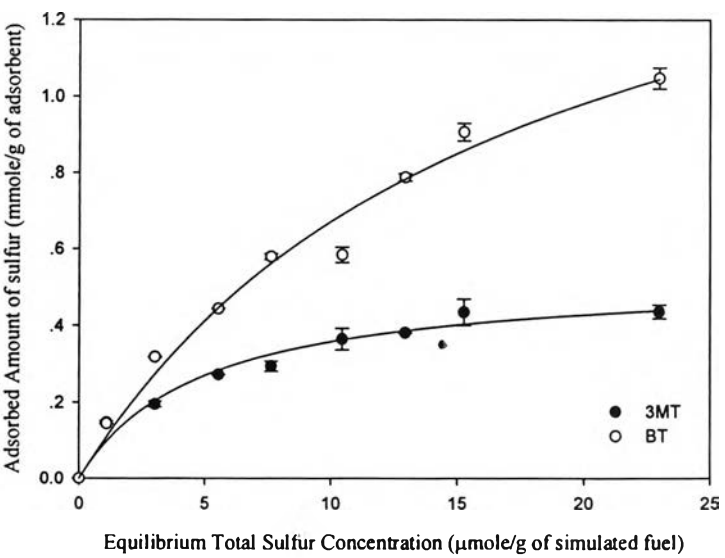

Figure 4.5 Adsorption isotherms of 3MT and BT on NaY zeolite in mixed-solute system at 25°C. Lines are curve-fitting using Langmuir isotherms.

Figures 4.6 and 4.7 show the comparison between the adsorption of 3MT in single and mixed systems on NaX and NaY zeolites, respectively. From the results, it can be obviously seen that adsorption of 3MT on both zeolites in the single system are much higher than mixed system. The mixed-solute system composed of 3MT and BT which are competitive components in the system. The results show that both zeolites prefer to adsorb BT selectively. It may be due to benzene funtional group in BT molecule. Both 3MT and BT are better adsorbed on NaX zeolite than NaY zeolite. The preferential adsorption observed here suggests that the NaX zeolite has more cation site and higher surface area than NaY zeolite. Figure 4.6 and 4.7 show the comparison between the adsorption of BT in single and mixed systems on NaX and NaY zeolites, respectively. From the Isotherms, it show that adsorption of BT on both zeolites in the single system are slightly higher than mixed system. It may be due to the preferential adsorption of BT on both zeolites as explained previously.

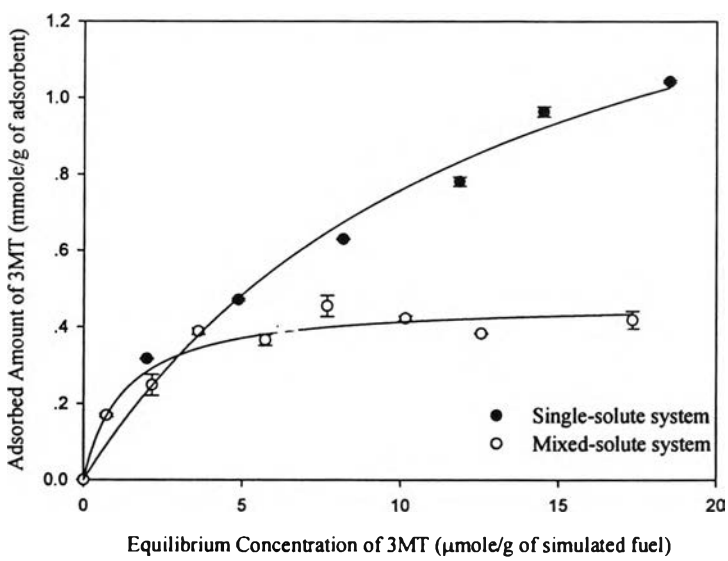

Figure 4.6 Adsorption isotherms of 3-methylthiophene on NaX zeolites in single and mixed-solue systems at 25°C. Lines are curve-fitting using Langmuir isotherms.

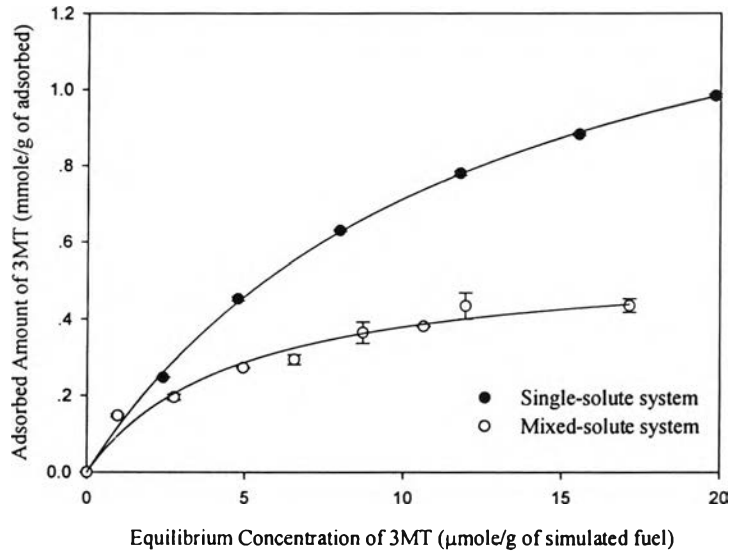

Figure 4.7 Adsorption isotherms of 3-methylthiophene on NaY zeolites in single and mixed-solute systems at 25°C. Lines are curve-fitting using Langmuir isotherms.

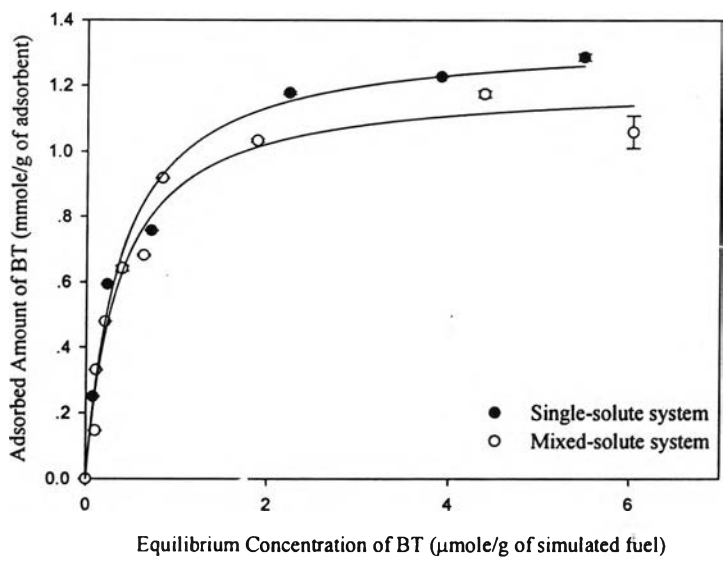

Figure 4.8 Adsorption isotherms of benzothiophene on NaX zeolites in single and mixed-solute systems at 25°C. Lines are curve-fitting using Langmuir isotherms.

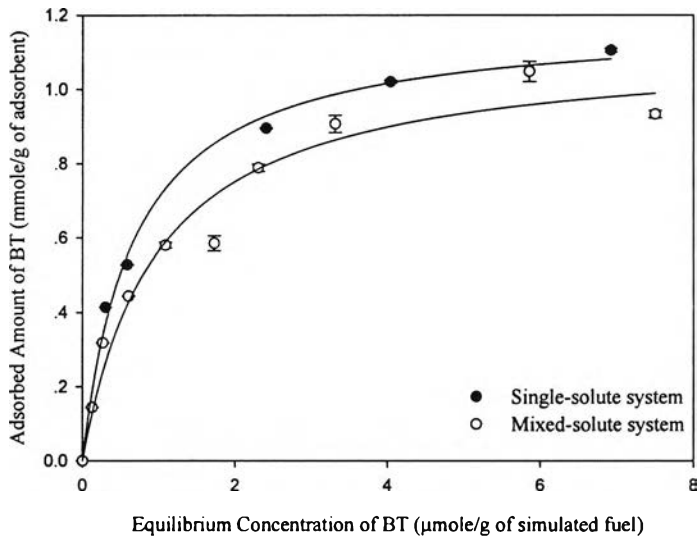

Figure 4.9 Adsorption isotherms of benzothiophene on NaY zeolites in single and mixed-solute systems at 25°C. Lines are curve-fitting using Langmuir isotherms.

4.2 Effect of Aromatic Content in Transportation Fuels on Sulfur Compounds Adsorption

The effect of aromatic content (*o*-xylene) in transportation fuels on 3MT, BT, and DBT adsorption by NaX and NaY zeolites was studied by using *o*-xylene at various concentration (0%, 4%, 8%, 12% and 16% by weight). The results are shown in Figures 4.10 to 4.12. Y-axis represents the amount of sulfur compounds adsorbed on zeolite and X-axis represents the percentage of aromatic content in transportation fuels. The aromatic compound used in this work was *o*-xylene. From the results, the adsorption of 3MT, BT, and DBT decreases significantly with increasing percentage of aromatic content, especially in the range of aromatic contents between 0-5%. This result shows that *o*-xylene can compete with three sulfur compounds in each system to adsorb on the zeolite surface. This may be the result of benzo functional group in *o*-xylene's structure. For trend of 3MT adsorption, the amount of 3MT adsorbed decrease considerably. This is due to the fact that *o*-xylene has π-electron in the benzene ring that can polarize on the zeolite surface. So o-xylene can adsorb on both zeolites better than 3MT.

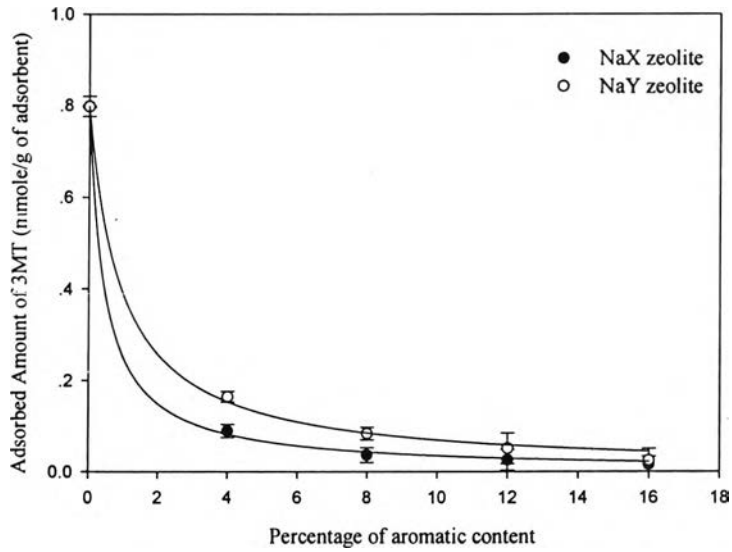

Figure 4.10 Effect of aromatic content on 3-metylthiophene adsorption on NaX and NaY zeolites.

Furthermore, both BT and DBT were adsorbed on NaX zeolite more than NaY zeolite in the mixed aromatic system. This result indicated that NaX zeolite has higher adsorption site when compared to NaY zeolite. More *o*-xylene was adsorbed on both NaX and NaY zeolite than BT and DBT. This is likely due to the effects of the size and the molecular structure of the solute. The molecule of *o*-xylene is smaller than both BT and DBT molecule so *o*-xylene can pass through the pore of the zeolite to adsorb on the adsroption site easily.

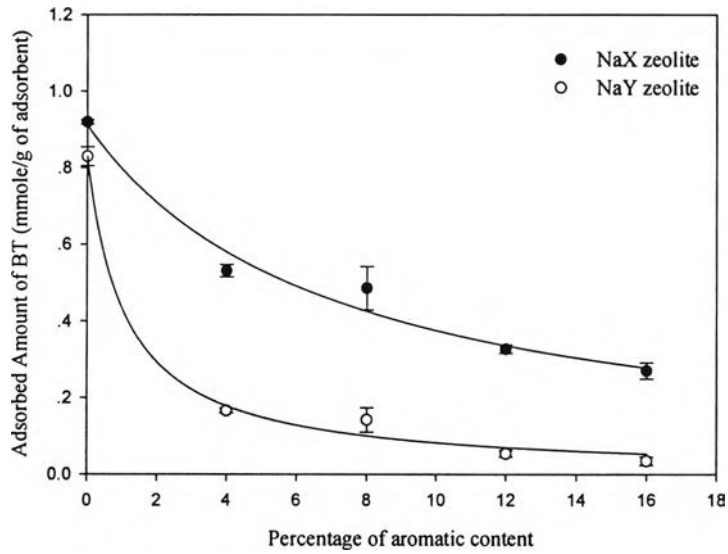

Figure 4.11 Effect of aromatic content on benzothiophene adsorption on NaX and NaY zeolites.

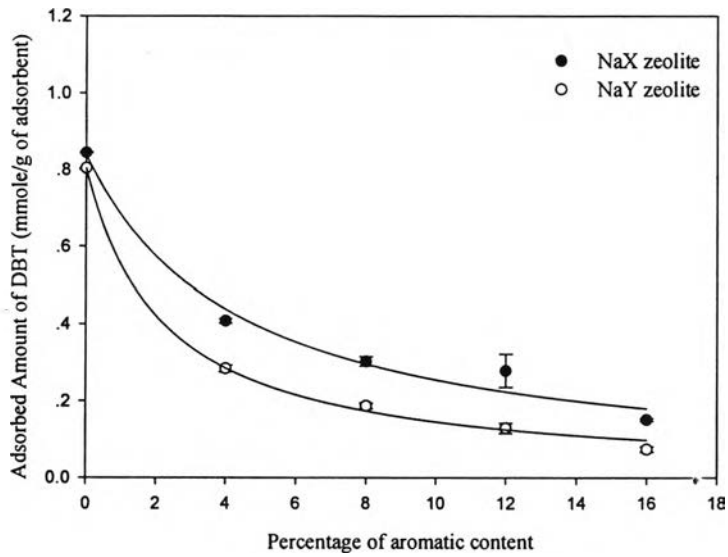

Figure 4.12 Effect of aromatic content on dibenzothiophene adsorption on NaX and NaY zeolites.

4.3 Effect of Water Content in Zeolite on Sulfur Compounds Adsorption

In order to investigate the effect of the water content in the zeolite, the adsorption of all 3 sulfur compounds was studied at 4 different percentage of water content in the zeolite, 0, 1.5, 3.0 and 4.5 as shown in Figures 4.13 to 4.15. Y-axis represents the amount of three sulfurs adsorbed on zeolite and X-axis represents the percentage of water content in the zeolite. From the results, the adsorption of 3MT, BT, and DBT decreases with increasing percentage of water content in the zeolite. This is because the adsorption sites of zeolites are preoccupied by water molecules. The adsorbed water molecules can be adsorbed on the cation sites of the zeolite and form a monolayer on the walls of the supercages by hydrogen bonds between water molecules and oxygen atoms of the zeolitic framework (Moise *et al.*, 2001), leading to a decrease in the adsorption capacity of both zeolites. Moreover, the adsorption of three sulfur compounds decreases significantly, especially in the range of water content between 0-3%. This may be explained that the adsorbed water molecules in this range occupied the initial surface area of zeolitic framwork so it has direct effect to the amount of sulfur adsorbed. For the comparison between NaX and NaY zeolites, it is found that the adsorption of all sulfur compounds on NaY zeolite decrease more than on NaX zeolite. This may be due to the fact that the NaX zeolite has higher cumulative pore volume when compared to NaY zeolite as shown in Table 4.2.

Table 4.2 The physical properties of faujasite zeolites

Faujasite Zeolite	Aperture (Å)	Si/Al ratio	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Water content (%wt)
NaX	7.4	1-1.5	580	0.5038	20.43
NaY	7.4	1.5-2.5	549	0.4720	19.17

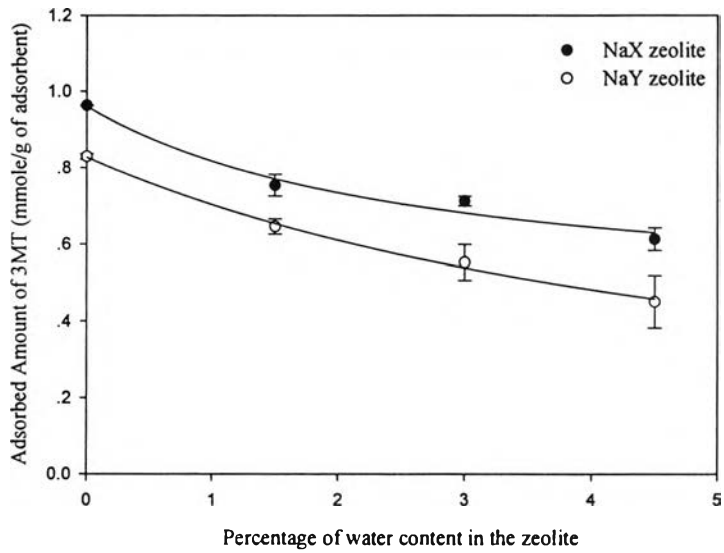

Figure 4.13 Effect of water content in zeolite on 3-metylthiophene adsorption on NaX and NaY zeolites.

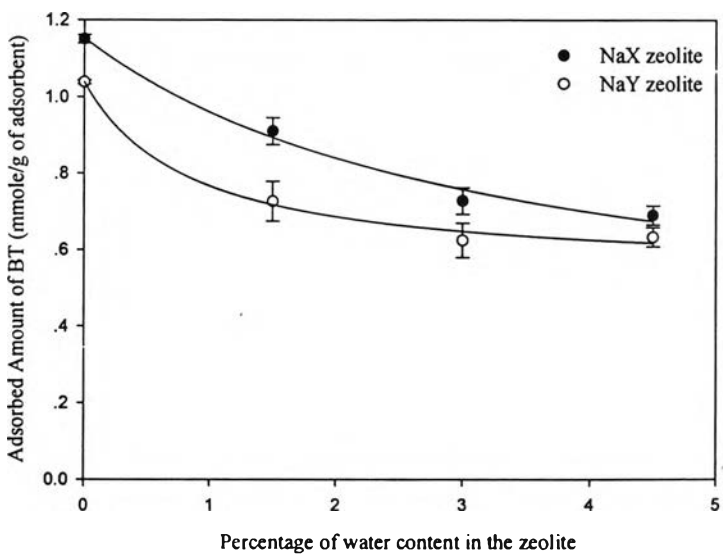

Figure 4.14 Effect of water content in zeolite on benzothiophene adsorption on NaX and NaY zeolites.

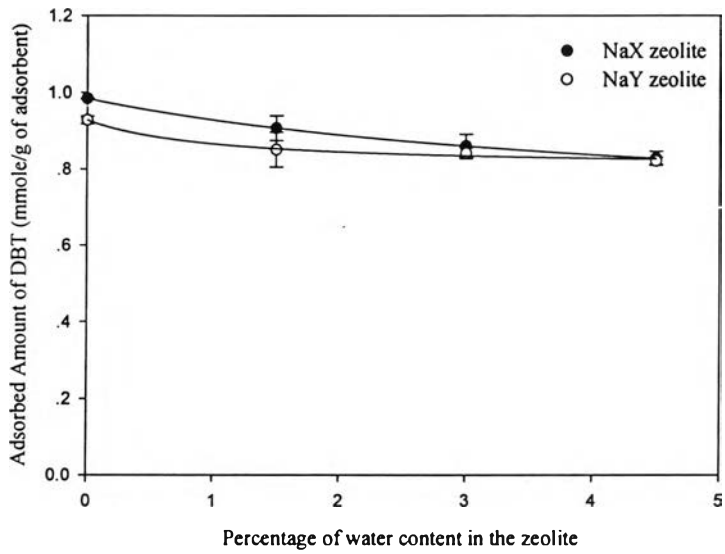

Figure 4.15 Effect of water content in zeolite on dibenzothiophene adsorption on NaX and NaY zeolites.

4.4 Effect of Temperature on Sulfur Compounds desorption

The effect of temperature on 3MT, BT, and DBT desorption was studied on NaX and NaY zeolites at 45, 60, and 75 degree centigrade as shown in Figures 4.16 to 4.18. Y-axis represents the amount of sulfur compounds desorbed and X-axis represents the desorption temperature. The results reveal that the desorption of 3MT, BT, and DBT increase with increasing temperature. The explanation to the adsorption amount decreases with increasing temperature come from the fundermental of adsorption which is the concept of equlibrium constant and Arenius's equation. Since the equlibrium constant decreases when increasing temperature. In addition, it can be obviously seen that when comparing between NaX and NaY, the increasing in the desorption of sulfur compounds from both zeolites and ability to desorb sulfur compounds are likely. This may be due to at high temperature, the higher sorption sites in NaX are not almost all available because the bonding between the sulfur compounds and sorption site is not strong enough. Moreover, the desorption of 3MT is 46% of the amount initially adsorbed

on both NaX and NaY zeolites at 25 °C and desorption of BT and DBT are about 16% and 8%, respectively. From the results, it was observed that the increase of 3MT desorption is much higher when compared to BT and DBT. This result agree well with the results in the adsorption studies that the bonding between 3MT and sorption sites is weaker when compared to BT and DBT adsorption on the zeolites. This is attributed to the presence of benzene funtional group in BT and DBT's structure.

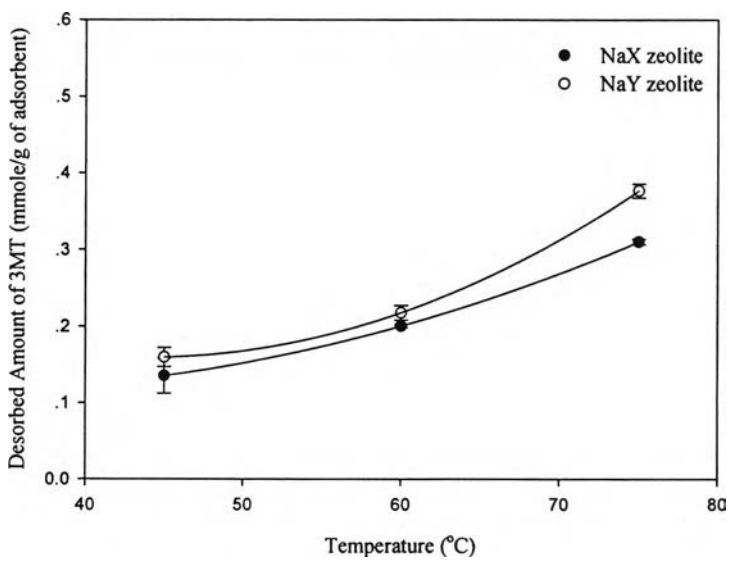

Figure 4.16 Effect of temperature on 3-metylthiophene desorption on NaX and NaY zeolites.

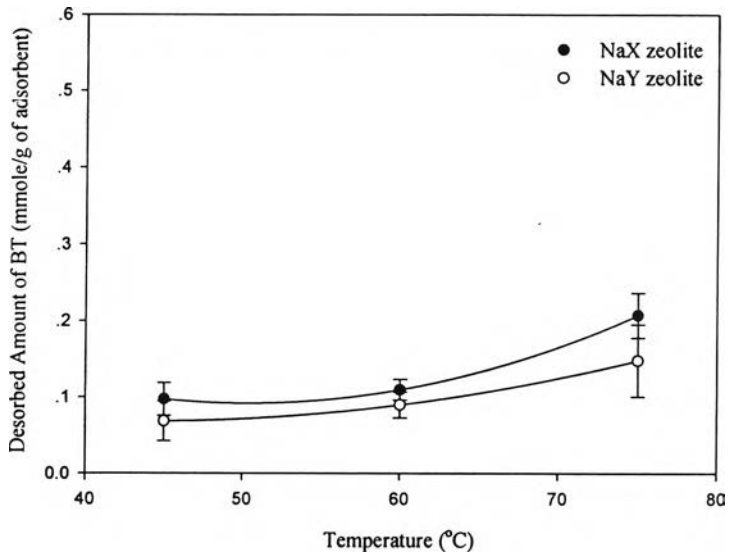

Figure 4.17 Effect of temperature on benzothiophene desorption on NaX and NaY zeolites.

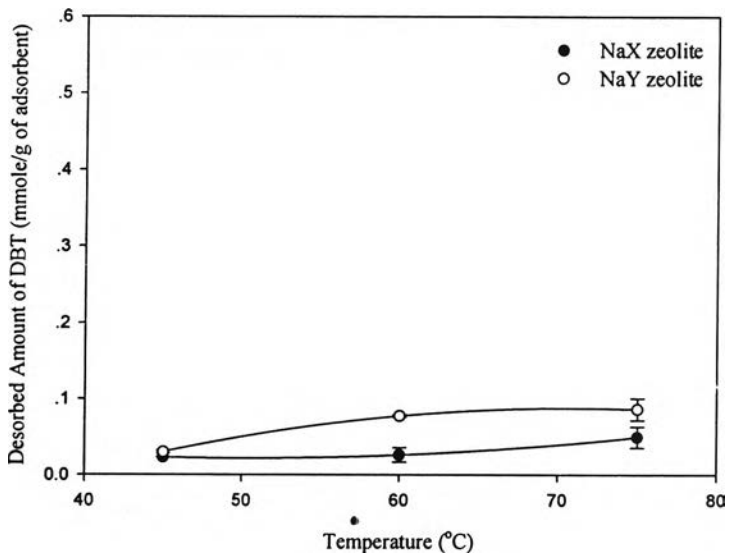

Figure 4.18 Effect of temperature on dibenzothiophene desorption on NaX and NaY zeolites.