

CHAPTER IV

RESULTS AND DISCUSSION

1. BET RESULTS

The BET results were shown in Table 4.1. 13X had the greatest BET surface area and pore volumes whereas 4A had the smallest. H-form of ZSM-5 had more surface area than other forms of ZSM-5 because of the size of ions which were 1×10^{-5} , 0.97 and 1.43 Å for H^+ , Na^+ and NH_4^+ , respectively.

Table 4-1 BET results

| No. | SAMPLE | BET surface area (m^2/g) | volume (cm^3/g) | |
|-----|---------------|------------------------------|------------------------------|-----------------|
| | | | single point total pore vol. | micro pore vol. |
| 1 | 13X | 481.1324 | 0.309802 | 0.202952 |
| 2 | HZSM-5 | 365.4437 | 0.236180 | 0.092251 |
| 3 | NaZSM-5 | 276.2554 | 0.196349 | 0.085690 |
| 4 | NH_4 ZSM-5 | 253.2480 | 0.175819 | 0.078135 |
| 5 | commercial 4A | 25.2971 | 0.088676 | 0.001213 |

2. EVALUATION OF MOMENTS OF THE CHROMATOGRAM

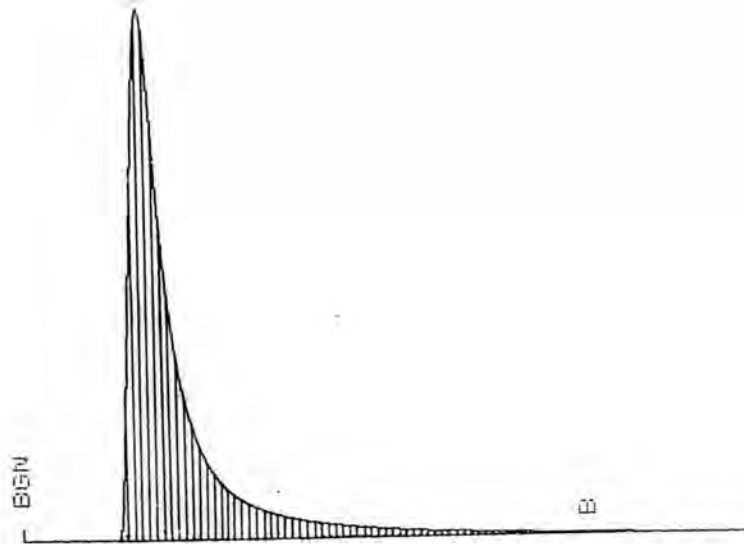


Figure 4-1 Chromatogram of the experiment result

Figure 4-1 shows an example of experimental chromatogram of the effluent from the adsorption column. The chromatogram was divided into small sliced area in order to determine the zero moment or the area of the chromatogram, the first absolute and second central moments from the following equations, respectively.

$$\text{zero moment :} \quad \text{area} \cong \sum c_i \Delta t_i \quad \text{---(4-1)}$$

$$\text{first absolute moment :} \quad t_R \cong \frac{\sum t_i c_i \Delta t_i}{\sum c_i \Delta t_i} \quad \text{---(4-2)}$$

$$\text{second central moment:} \quad \sigma^2 \cong \frac{\sum (t_i - t_R)^2 c_i \Delta t_i}{\sum c_i \Delta t_i} = \frac{\sum t_i^2 c_i \Delta t_i}{\sum c_i \Delta t_i} - t_R^2 \quad \text{---(4-3)}$$

3. FIRST MOMENT RESULTS

A necessary condition of the mathematical description of the adsorption process was that the adsorption isotherm was linear. The adsorption measurements were made at sufficiently low concentrations. In order to verify such condition, the first moment measurements were made by varying the amounts of injection. Both shape of the chromatograms and the weighted mean retention times were similar for the amounts of injection of 50 - 250 μl as shown in Figure 4-2. Thus, the sample gas obeyed the dilute gas assumption and the linear isotherm was also valid for all experiments.

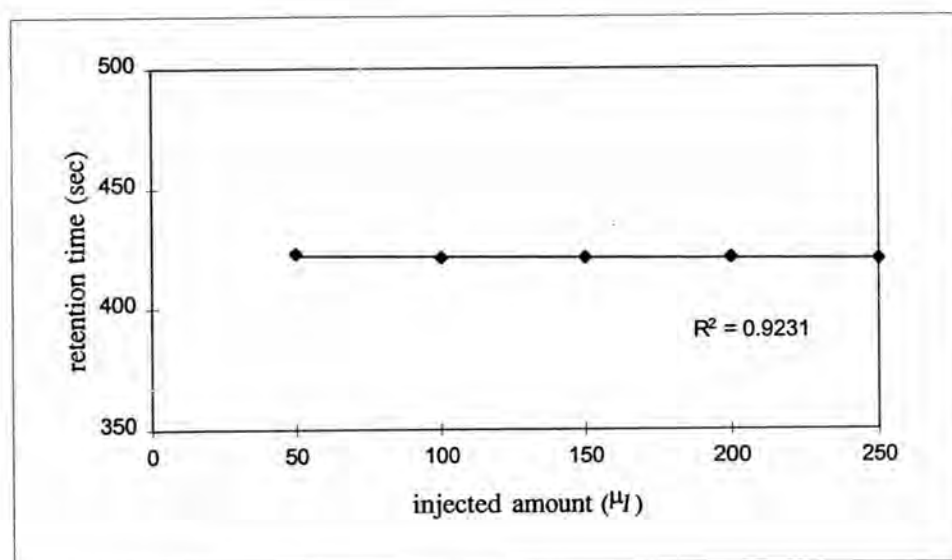


Figure 4-2 The linearity of the weighted mean retention time

Injected amount had to be varied in order to achieve the appropriate chromatograms which could be analyzed precisely.

Figure 4-3 and 4-4 illustrated the plots of weighted mean retention time (t_R) for toluene and o-xylene vapors, respectively. All results were straight line of which the adsorption equilibrium constant (K) were able to be determined from the slope of the corresponding line according to equation 2-19. The adsorption equilibrium constants of toluene and o-xylene were summarized in Table 4-2.

The retention time of each chromatogram was affected by two parameters, i.e. the adsorption equilibrium constant and the carrier gas velocity. In principle, the retention time became longer with a large value of the equilibrium constant than with a small one for a given gas velocity. In contrast, it became shorter with a high flow rate than the slow one for a given the adsorption equilibrium constant.

As effects of temperatures, the retention time decreased as an increase in temperature for a given flow rate. In other words, the adsorption equilibrium constant became smaller at high temperature than at low temperature. the results corresponded to exothermic process. The adsorption, thus, was physical adsorption.

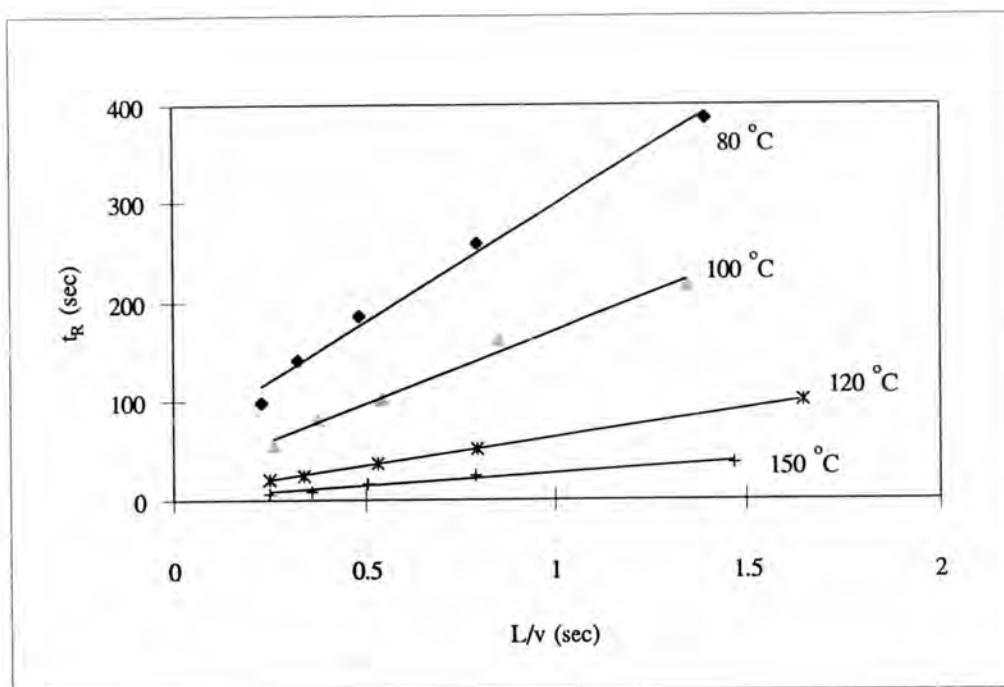


Figure 4-3 Weighted mean retention time of toluene on synthesized 4A

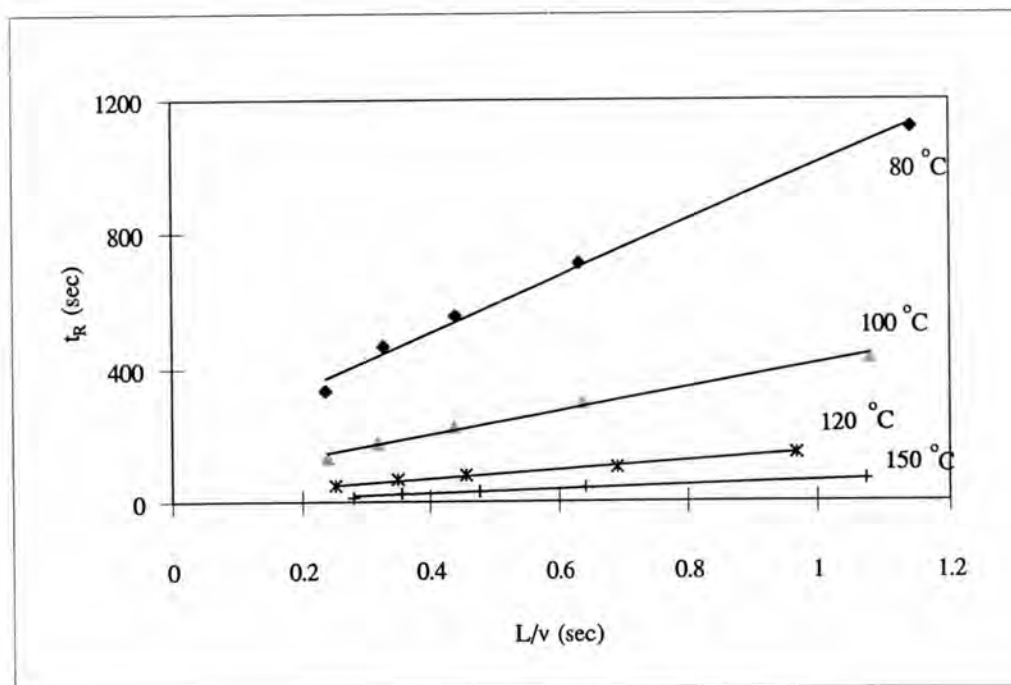


Figure 4-4 Weighted mean retention time of o-xylene on synthesized 4A

Table 4-2 Adsorption equilibrium constants of toluene and o-xylene

| Adsorbent | Temperature (°C) | K * | |
|-----------------------|---------------------|-----------------------|--------------------|
| | | Toluene | O-xylene |
| commercial 4A | 80 | 1.37×10^3 | 7.67×10^3 |
| | 100 | 3.87×10^2 | 2.44×10^3 |
| | 120 | 2.54×10^2 | 1.17×10^3 |
| | 150 | 1.80×10^2 | 1.95×10^2 |
| | 175 | - | 1.35×10^2 |
| synthesized 4A | 80 | 2.03×10^2 | 7.13×10^2 |
| | 100 | 1.24×10^2 | 2.98×10^2 |
| | 120 | 4.76×10 | 1.13×10^2 |
| | 150 | 2.03×10 | 5.00×10 |
| NaZSM-5 | 80 | 7.27×10^3 | 3.65×10^3 |
| | 100 | 5.03×10^3 | 1.67×10^3 |
| | 120 | 1.42×10^3 | 1.17×10^3 |
| NH ₄ ZSM-5 | 120 | 4.06×10^4 ** | 8.79×10^3 |
| | 150 | 2.02×10^4 | 6.21×10^3 |
| | 175 | 1.44×10^4 | 3.89×10^3 |
| | 200 | 8.14×10^3 | 2.15×10^3 |
| HZSM-5 | 120 | 4.85×10^4 ** | 1.04×10^4 |
| | 150 | 1.82×10^4 | 8.15×10^3 |
| | 175 | 7.93×10^4 | 4.67×10^3 |
| | 200 | 4.52×10^3 | 3.47×10^3 |

Table 4-2 (continued)

| Adsorbent | Temperature (°C) | K * | |
|-----------|---------------------|-----------------------|--------------------|
| | | Toluene | O-xylene |
| 13X | 100 | - | 1.52×10^3 |
| | 120 | 2.06×10^5 ** | 9.03×10^2 |
| | 150 | 1.08×10^5 ** | 5.65×10^2 |
| | 175 | 6.74×10^4 | 4.50×10^2 |
| | 200 | 4.46×10^4 | 3.02×10^2 |
| | 225 | 3.03×10^4 | - |

* all adsorption equilibrium constants were expressed in dimensionless form : $((\text{mol}/\text{cm}^3 \text{ of pellet})/(\text{mol}/\text{cm}^3 \text{ of gas}))$

** extrapolating from experimental results

According to equation 2-19, the straight line should pass the origin but for some systems, especially for 4A packed in a longer tube than others, the intercepts clearly deviate from the origin. This was the effect of the deviation from isobaric condition within the bed (Carleton, 1978). The extrapolation of the asymptotic linearity to infinite flow rate led the first moment are equal to zero on the negative-axis. It depended only on the parameters of the packed bed and the viscosity of the carrier gas but it was independent of the nature of the adsorbed species.

The correlation between the adsorption equilibrium constant and the column temperature obeyed the van't Hoff equation. In other words, the logarithmic of equilibrium constant was proportionate to the reciprocal temperature. Then the heat of adsorption was able to be obtained from the slope of the linear plot. In addition, the resulted heat of adsorption was independent of temperature.

For a given adsorbate, the heat of adsorption on each type of adsorbents, as summarized in Table 4-3, was different from others owing to their surface chemistry. It might be higher or lower than heat of condensation at the normal boiling point of the adsorbate.

Table 4-3 Heat of adsorption of toluene and o-xylene on zeolites

| Adsorbent | Heat of Adsorption (kJ/mol) | |
|-----------------------|-----------------------------|----------|
| | Toluene | O-xylene |
| commercial 4A | -34.66 | -58.47 |
| synthesized 4A | -42.10 | -48.00 |
| NaZSM-5 | -46.50 | -33.06 |
| NH ₄ ZSM-5 | -30.22 | -26.88 |
| HZSM-5 | -46.57 | -22.06 |
| 13X | -29.66 | -22.56 |

Interestingly, the heat of adsorption of a given adsorbate decreased when the equilibrium constant of the same adsorbate became large since the high adsorption ability adsorbent released small amount of energy when the system reached the equilibrium whereas the low ability adsorbent needed to release more energy to achieve the equilibrium.

Heat of adsorption was one of parameters which had to be considered for selecting an appropriate adsorbent. Adsorbent which released small amount of heat of adsorption became advantage because the energy required in the regeneration step of adsorption process was low.

1.) Effects of Binder

Since commercial zeolite molecular sieves, i.e. 4A and 13X were composed of aluminosilicate crystals and some types of activated clays as a binder. Their effects on adsorption of toluene and o-xylene were studied with Union Carbide 4A (including binder) and synthesized 4A (without binder). Both amount of toluene and o-xylene vapors adsorbed on the commercial one were much larger than that on the synthesized one, as shown in Figure 4-5 and 4-6, respectively. These results illustrated that a large fraction of both toluene and o-xylene vapors were adsorbed on the binder. Furthermore, both vapors diffused into the 4A crystals difficultly since the pore size of the 4A crystal was smaller than the average molecular sizes of the adsorbates.

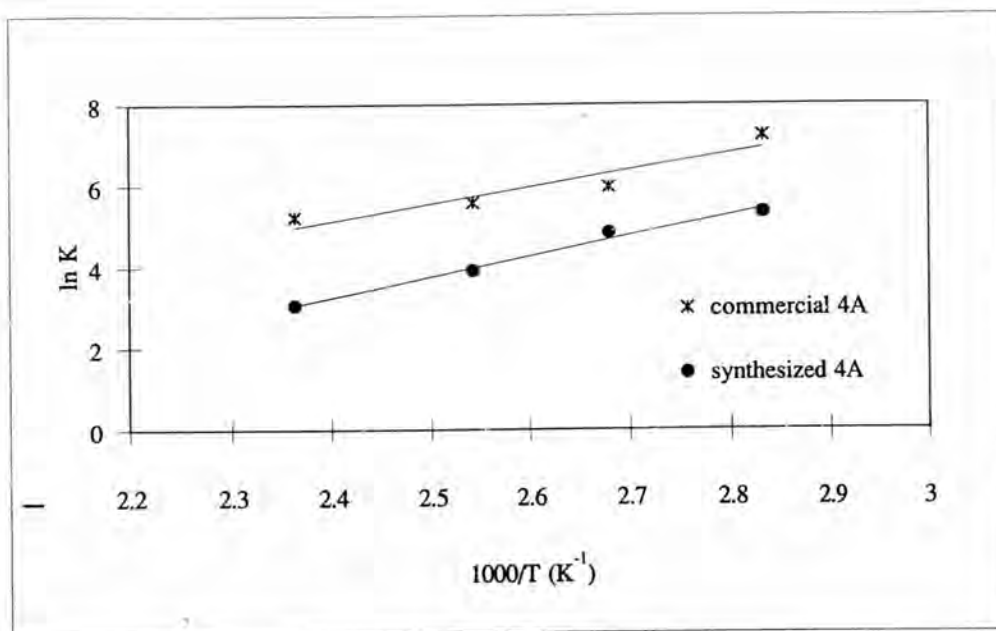


Figure 4-5 Comparison of adsorption equilibrium constants of toluene on commercial 4A and synthesized 4A

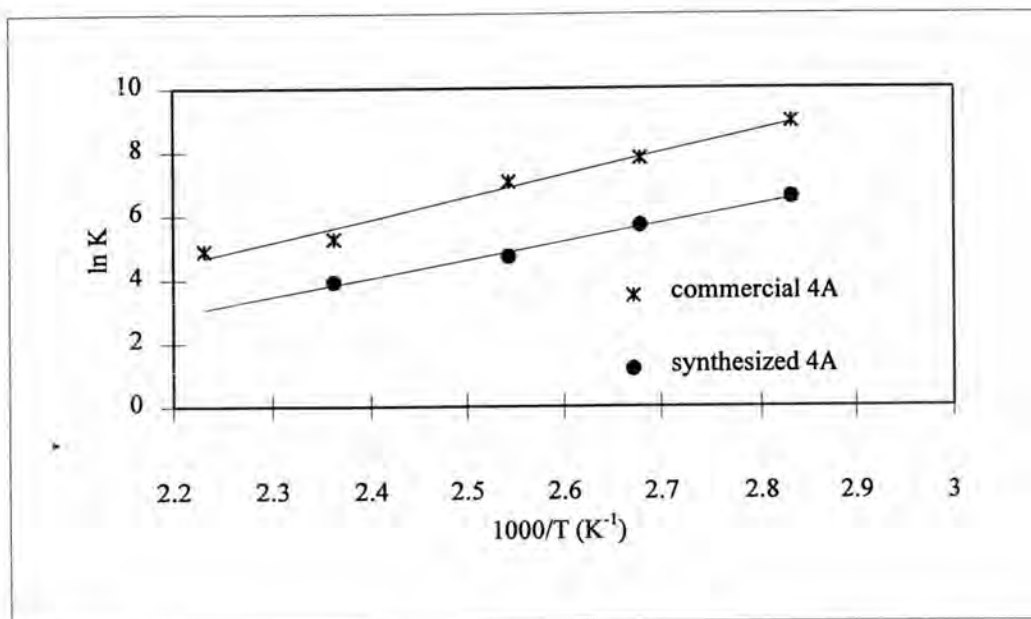


Figure 4-6 Comparison of adsorption equilibrium constants of o-xylene on commercial 4A and synthesized 4A

2.) Effects of Structure of Zeolite

2.1) Toluene

The influence of different pore sizes of 4A, NaZSM-5 and 13X caused their different toluene adsorption abilities. 13X, the largest pore size zeolite, had the highest adsorption equilibrium constants while 4A with smallest pore size had the lowest equilibrium constants, as illustrated in Figure 4-7. The adsorption equilibrium constant of NaZSM-5 which was synthesized without binder was higher than that of commercial 4A. This indicated that the effect of binder on adsorption equilibrium was lower than the effect of pore size.

2.2) O-xylene

Considered the o-xylene adsorption equilibrium constants in Figure 4-8, the equilibrium constants of synthesized 4A were the lowest. At high temperature, the equilibrium constants of commercial 4A were lower than that of 13X and ZSM-5 because of the effect of pore size but they became similar at low temperature. Effects of temperature on each system were different. It depended on the interaction of each pair of adsorbate-adsorbent. Therefore, heat of adsorption and the dependence of the adsorption equilibrium constant upon temperatures for each system became different from another.

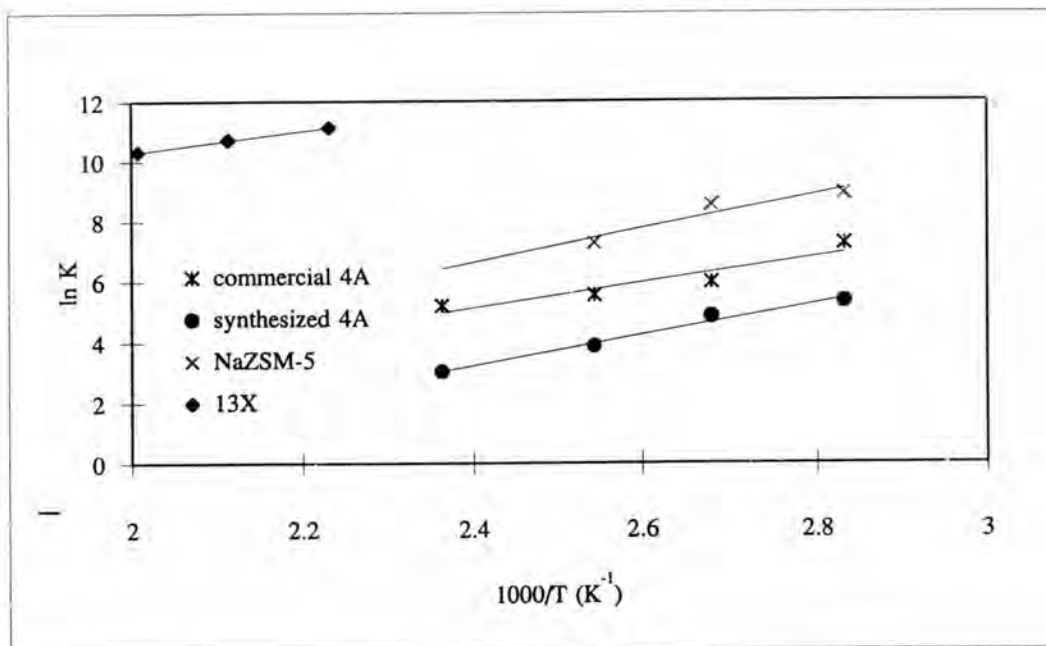


Figure 4-7 comparison of adsorption equilibrium constants of toluene on 4A , NaZSM-5 and 13X

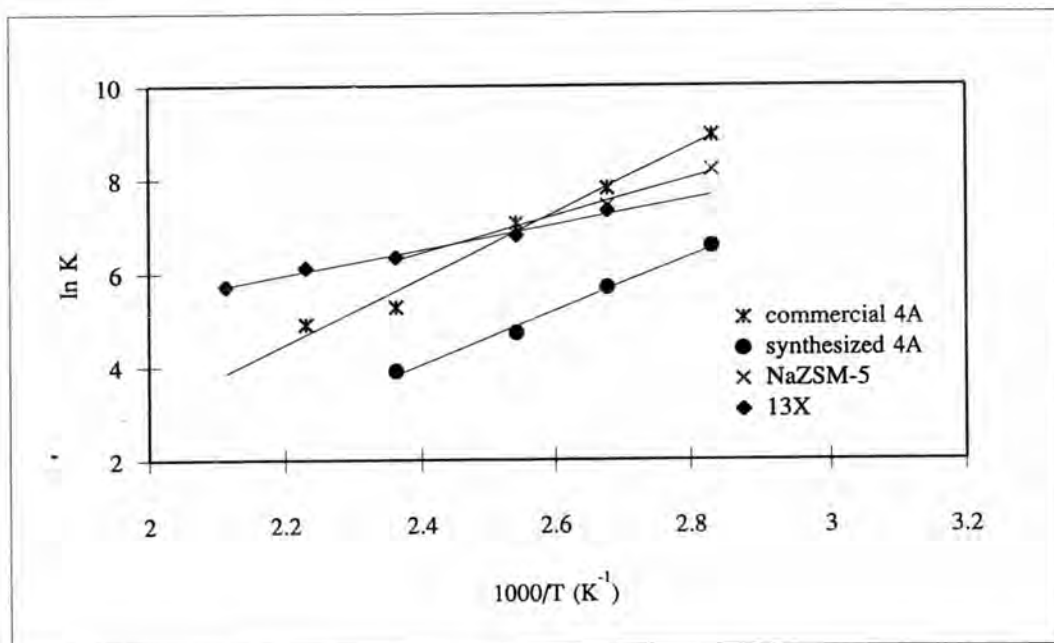


Figure 4-8 comparison of adsorption equilibrium constants of o-xylene on 4A , NaZSM-5 and 13X

The adsorption equilibrium constants of toluene and o-xylene vapors on the same zeolites were compared. They were found that the equilibrium constants of toluene were higher than that of o-xylene. Toluene was able to be adsorbed more easily than o-xylene because it contained only one methyl group which caused the smaller molecular size and shorter molecular length. For synthesized zeolites, i.e. ZSM-5 and 4A, the adsorption equilibrium of toluene and o-xylene were almost equal. However, for commercial zeolites, i.e. 13X and Union Carbide 4A, the equilibrium constants became much different because in synthesized zeolites, the adsorption occurred only at the crystals, while in commercial zeolite, the adsorbates were adsorbed on both the crystals and binder.

3.) Effects of Types of Cations

Figure 4-9 and 4-10 showed the same trend for both toluene and o-xylene vapors adsorbed on NaZSM-5, NH₄ZSM-5 and HZSM-5. The adsorption equilibrium constants of Na-form were much lower than that of NH₄-form and H-form, while the equilibrium constants of NH₄-form and H-form were almost equal. The electronegativities of sodium and hydrogen are 0.9 and 2.1, respectively. The surface of HZSM-5 and NH₄ZSM-5 frameworks consisted of the hydrogen atom bonded with oxygen atom, thus, HZSM-5 and NH₄ZSM-5 were able to adsorb toluene and o-xylene vapors better than NaZSM-5. The sizes of ions: H⁺, Na⁺ and NH₄⁺ did not

affect the adsorption ability of toluene and o-xylene. These results differed from N_2 adsorption of which that the adsorption ability also depended on the size of ions. The form of ZSM-5 with smallest ion size, H^+ , adsorbed N_2 the best but the adsorption on the largest ion, i.e. NH_4^+ , became the worst. This showed that the effects of types of cations appeared in combination with certain adsorbates depending upon at least physical properties, such as molecular sizes, polarities, etc.

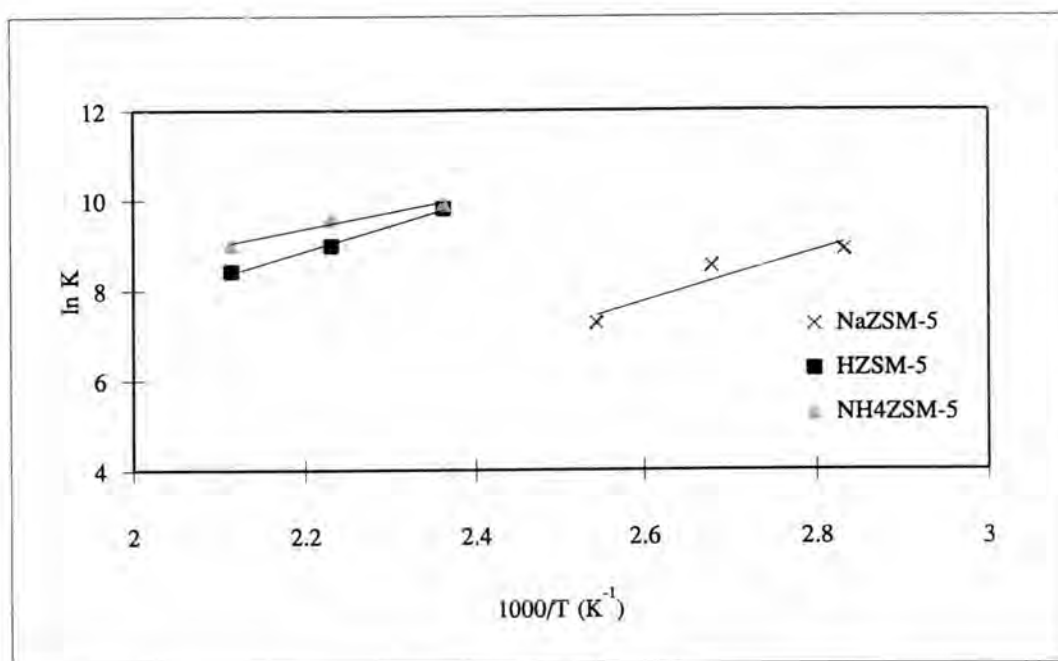


Figure 4-9 comparison of adsorption equilibrium constants of toluene on HZSM-5, NaZSM-5 and NH_4ZSM-5

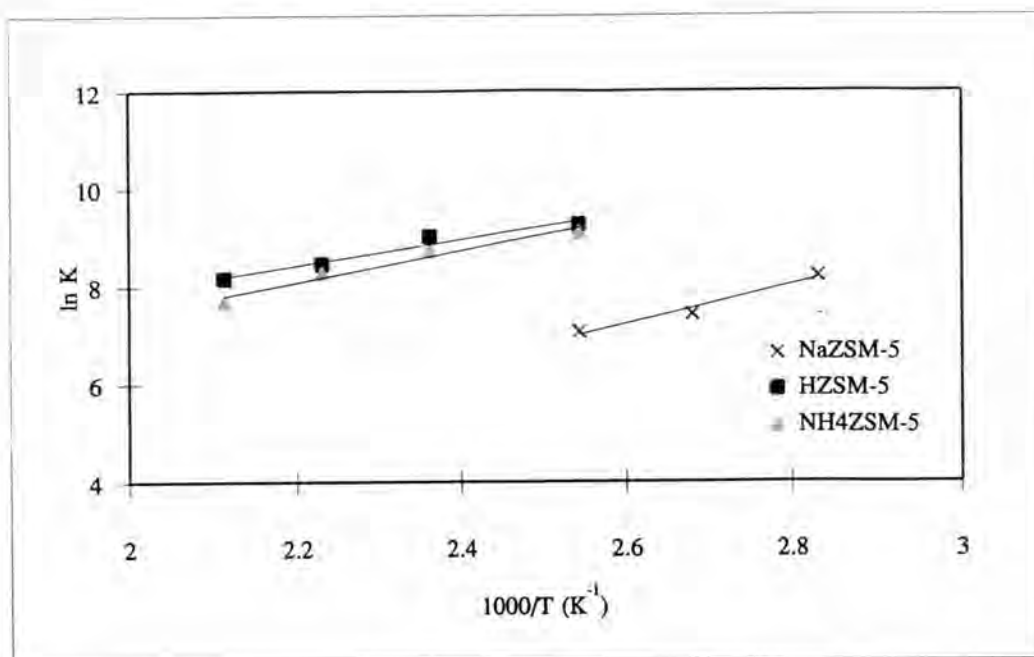


Figure 4-10 comparison of adsorption equilibrium constants of o-xylene on HZSM-5, NaZSM-5 and NH₄ZSM-5

The results of the adsorption equilibrium constants of toluene vapor adsorbed on 13X of this experiment were compared with the previous studies (Ruthven and Kaul, 1993), as illustrated in Table 4-4. The equilibrium constants measured by gravimetric method were obtained from the slopes in the low concentration region of the Langmuir isotherm at pressure 0.1 - 100 torr as shown in Figure 4-11. The interpolated equilibrium constants by gravimetric method at temperature 200 and 225 °C were found to be higher than the results of this research about one order of magnitude. This difference occurred since the results by gravimetric method could not be done at actually low concentration. Then, they needed to be approximated. In addition, the basis of the measurements, i.e. the amount adsorbed per units volume of

Table 4-4 The adsorption equilibrium constants of toluene on 13X by gravimetric and chromatographic method

| Temp. (°C) | Gravimetric (crystal volume basis) | Chromatographic (previous) (crystal volume basis) | Chromatographic (this work) (pellet volume basis) |
|---------------|---------------------------------------|---|---|
| 200 | 7.83×10^5 * | - | 4.46×10^4 |
| 225 | 2.68×10^5 * | - | 3.03×10^4 |
| 267 | - | 5.4×10^4 | 1.74×10^4 ** |
| 289 | - | 2.7×10^4 | 1.35×10^4 ** |
| 308 | - | 1.5×10^4 | 1.09×10^4 ** |
| 322 | - | 1.0×10^4 | 9.47×10^3 ** |

* interpolated

** extrapolated

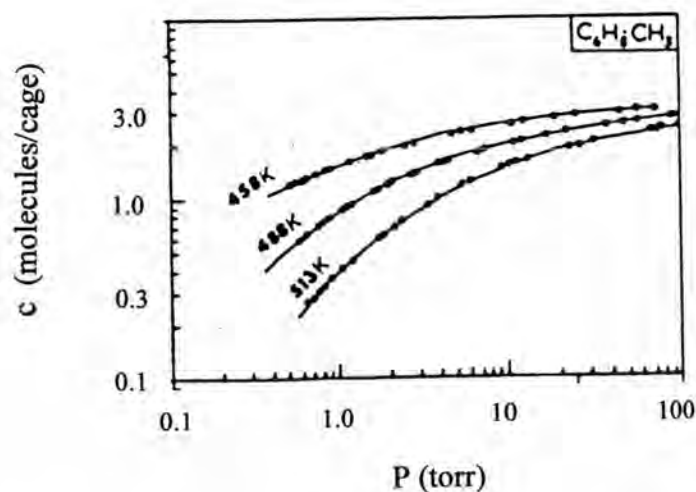


Figure 4-11 Langmuir isotherm of toluene adsorbed on 13X by gravimetric method

crystal and per unit volume of pellet, respectively, were different. It was also impossible to estimate the amount adsorbed per unit volume of crystal from that of pellet due to lack of information of content of binder in commercial 13X.

Based on the chromatographic experiments, the comparison of adsorption equilibrium constants had to be compared at the same temperature. Since the experiments were carried out in the different range of temperatures, the adsorption equilibrium constants had to be estimated at the same range of temperature with the assumption of constant heat of adsorption according to the van't Hoff equation. All results were in the same order of magnitude, as summarized in Table 4-4.

4. SECOND MOMENT RESULTS

4.1 Axial Dispersion

Figure 4-12 and 4-13 illustrated the axial dispersion coefficients of flow through all adsorbent beds for toluene and o-xylene, respectively. All the values of axial dispersion coefficients were not much different from one another and were in the same order of magnitude except for the synthesized 4A bed. Axial dispersion could not be affected by types of adsorbent but it could be affected by bed porosity.

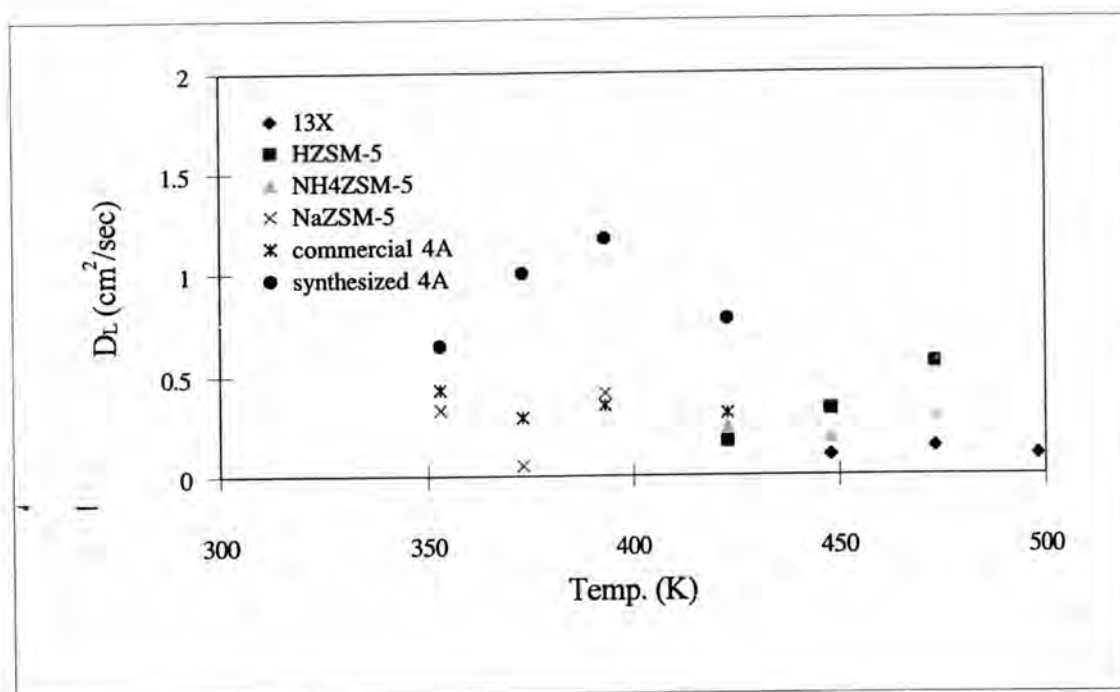


Figure 4-12 Axial dispersion of toluene vapor flow through packed bed

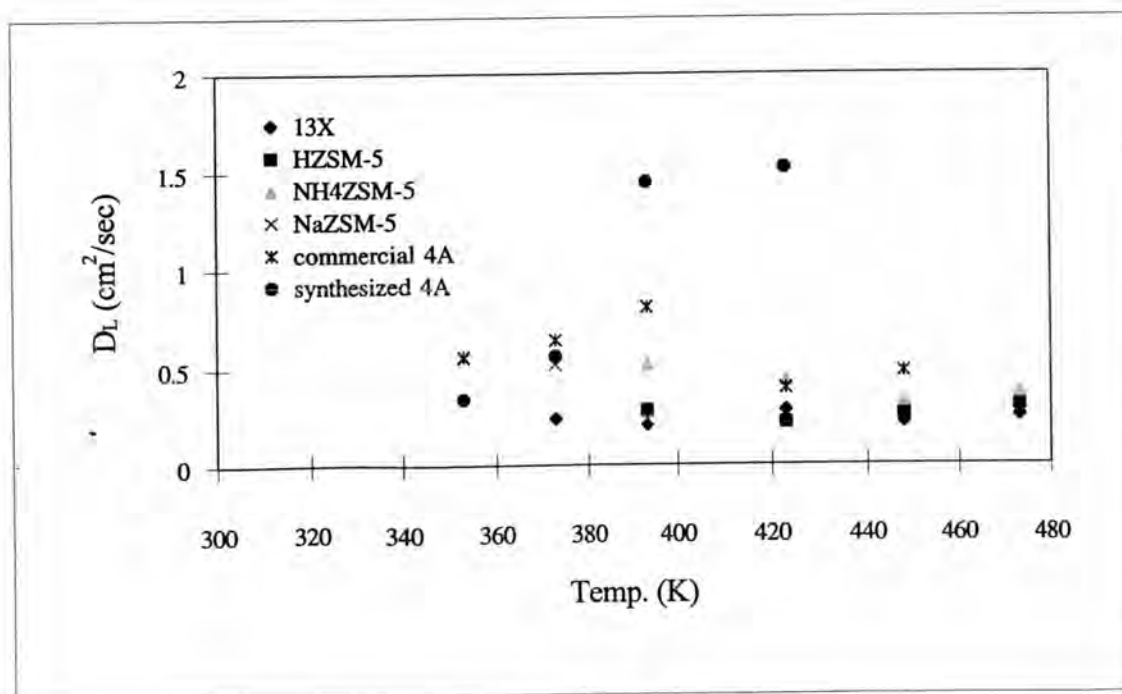


Figure 4-13 Axial dispersion of o-xylene vapor flow through packed bed

The axial dispersion coefficients of the synthesized 4A bed were higher than other beds because of the bed length. For the system which had very long bed lengths such as the study of Suzuki (1972), the axial dispersion coefficients of helium in hydrogen for the column lengths 100 and 200 cm were not different indicated that end effects were insignificant. But for the very short bed length, end effects became significant. For the rest of results, it was found that the axial dispersion became independent of temperature because of the relatively short bed length. In addition, the values of the axial dispersion were quite small in short bed length leading to insignificant effects of axial dispersion as reported by Eic and Ruthven (1988).

4.2 Overall Mass Transfer Coefficient

The overall mass transfer coefficients of toluene and o-xylene on zeolites at various temperature were summarized in Table 4-4.

Table 4-5 Overall mass transfer coefficients of toluene and o-xylene

| Adsorbent | Temperature (°C) | k (sec ⁻¹) | |
|-----------------------|---------------------|------------------------|-----------------------|
| | | Toluene | O-xylene |
| commercial 4A | 80 | 2.32×10^{-2} | 8.74×10^{-3} |
| | 100 | 6.30×10^{-2} | 1.77×10^{-2} |
| | 120 | 9.44×10^{-2} | 2.62×10^{-2} |
| | 150 | 1.85×10^{-1} | 9.77×10^{-2} |
| | 175 | - | 1.72×10^{-1} |
| synthesized 4A | 80 | 3.78×10^{-2} | 3.17×10^{-2} |
| | 100 | 3.38×10^{-2} | 4.50×10^{-2} |
| | 120 | 9.40×10^{-2} | 4.70×10^{-2} |
| | 150 | 4.05×10^{-1} | 5.22×10^{-2} |
| NaZSM-5 | 80 | 4.67×10^{-3} | 5.03×10^{-3} |
| | 100 | 4.35×10^{-3} | 8.87×10^{-3} |
| | 120 | 1.92×10^{-2} | 9.31×10^{-3} |
| NH ₄ ZSM-5 | 120 | - | 4.46×10^{-3} |
| | 150 | 1.19×10^{-2} | 6.18×10^{-3} |
| | 175 | 1.03×10^{-2} | 7.78×10^{-3} |
| | 200 | 1.88×10^{-2} | 9.72×10^{-3} |
| HZSM-5 | 120 | - | 6.52×10^{-3} |
| | 150 | 8.75×10^{-3} | 7.07×10^{-3} |
| | 175 | 1.67×10^{-2} | 8.44×10^{-3} |
| | 200 | 2.38×10^{-2} | 6.61×10^{-3} |

Table 4-5 (continued)

| Adsorbent | Temperature (°C) | k (sec ⁻¹) | |
|-----------|---------------------|------------------------|-----------------------|
| | | Toluene | O-xylene |
| 13X | 100 | - | 2.82×10^{-2} |
| | 120 | - | 5.37×10^{-2} |
| | 150 | - | 5.40×10^{-2} |
| | 175 | 1.27×10^{-2} | 1.09×10^{-1} |
| | 200 | 2.41×10^{-2} | 2.46×10^{-1} |
| | 225 | 2.02×10^{-2} | - |

The shape of chromatograms could, also, be used to explain mass transfer rates of the system. The chromatogram was almost symmetrical and sharp for high rate of mass transfer. For low mass transfer rate, molecules needed a longer period to transfer in and transfer out, therefore the chromatogram became broad and long peak tailing occurred. Figure 4-14 illustrated the chromatograms of toluene adsorbed on 13X and synthesized 4A.

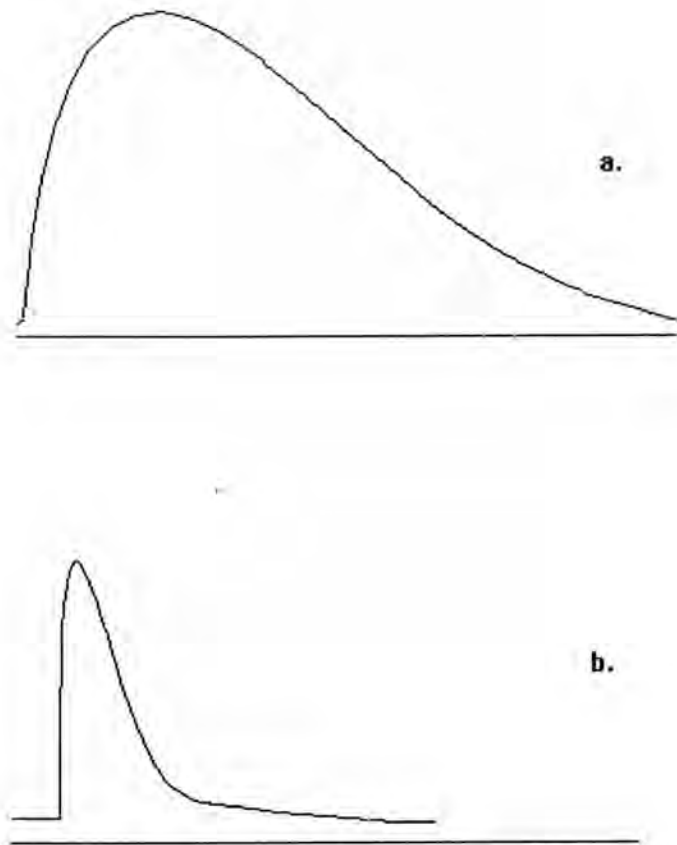


Figure 4-14 Shape of chromatograms a. toluene adsorbed on 13X

b. toluene adsorbed on synthesized 4A

In the similar way to Arrhenius' law, the overall mass transfer coefficient could be represented in the following expression :

$$k = k_0 e^{-E/RT} \quad \text{----- (4-5)}$$

The plots between the overall mass transfer coefficients and the reciprocal temperatures were illustrated in Figure 4-15 and 4-16.

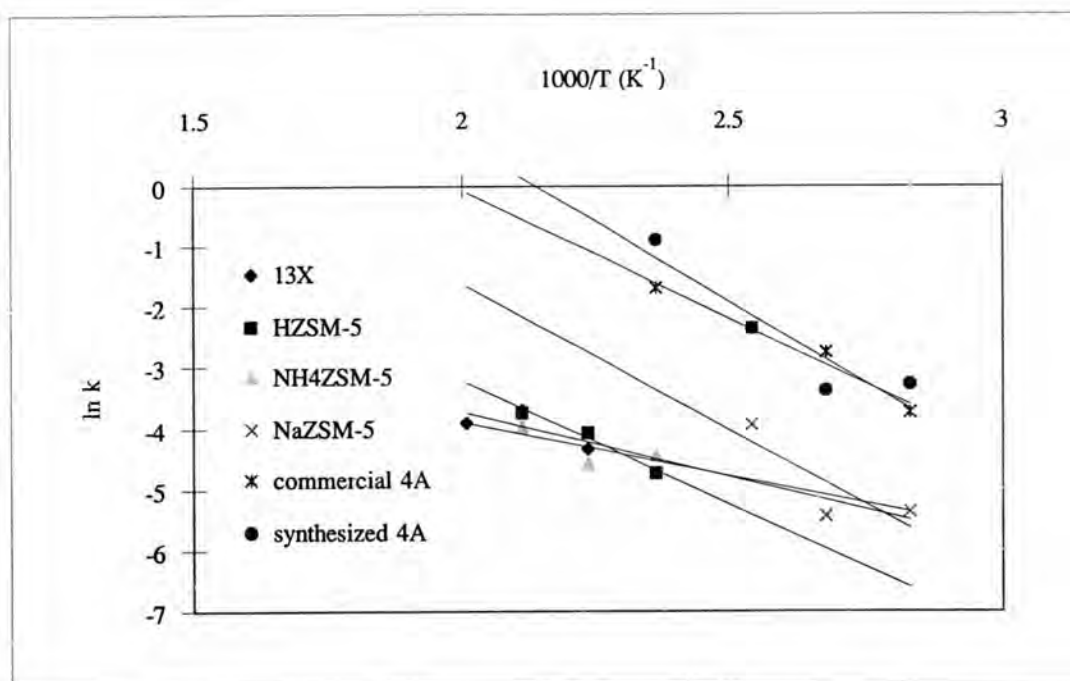


Figure 4-15 Overall mass transfer coefficients of toluene

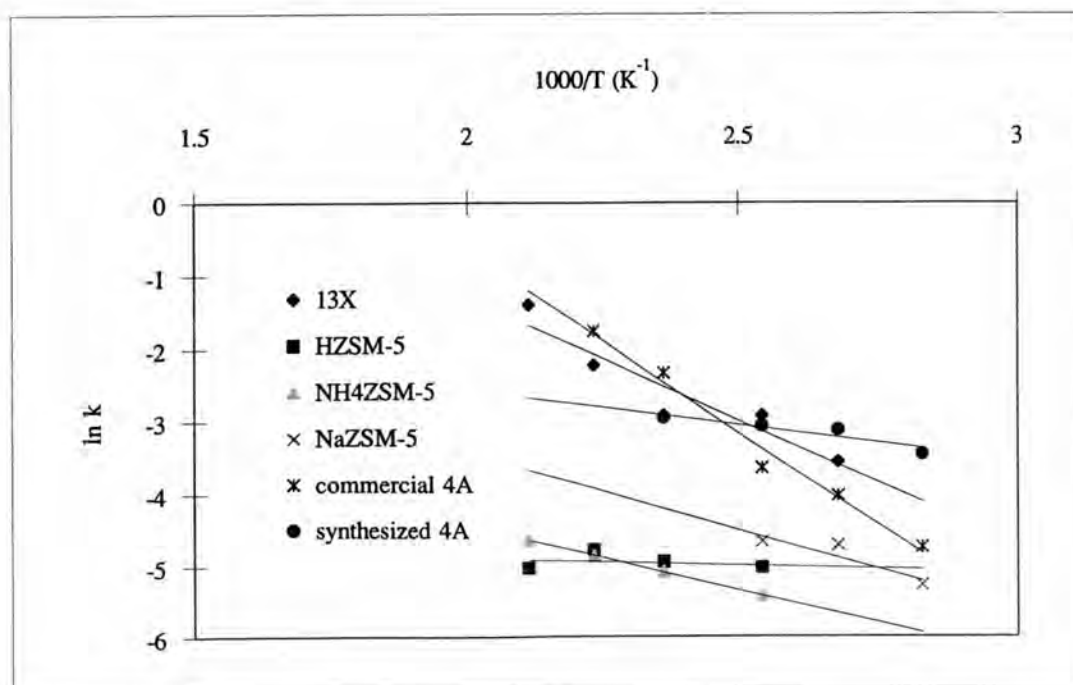


Figure 4-16 Overall mass transfer coefficients of o-xylene

In Figure 4-15, the overall mass transfer coefficients of toluene flowed through the 4A bed obeyed the Arrhenius' equation. They were proportionate to the reciprocal temperatures, while the overall mass transfer coefficients of toluene flowed through the ZSM-5 and 13X bed became independent of temperature.

For o-xylene, the overall mass transfer coefficients of synthesized zeolites, i.e. ZSM-5 and 4A, yielded the same results as those of toluene with ZSM-5 while, the coefficients of xylene with 13X were clearly proportionate to the reciprocal temperatures.

The resulted overall mass transfer coefficient included the external film mass transfer coefficient and pore mass transfer whereas the controlling step of each system was not verified.

The external film mass transfer coefficients calculated from Sherwood number in equation 2-6 were much higher than the overall mass transfer coefficients from the experimental results. Thus, the controlling step of mass transfer should be pore diffusion.

It was known that micropore size of 4A was smaller than the molecular sizes of toluene and o-xylene but the experiment results showed that the molecules of toluene and o-xylene were able to transfer through the 4A bed faster than other beds.

The rate of adsorption on 4A zeolites might be controlled by the macropore diffusion, while the controlling step of adsorption for other zeolites was the micropore diffusion.

The overall mass transfer coefficients of all types of ZSM-5 were in the same range. Thus, types of cation did not affect to the rate of adsorption. O-xylene transferred in 13X faster than in ZSM-5 due to shape and size of o-xylene which was difficult to diffuse through the pore of ZSM-5. While the mass transfer coefficients of toluene in ZSM-5 and 13X were in the same range since the molecule of toluene was smaller than o-xylene. Then, toluene could diffuse through the pore of ZSM-5 at the similar rate to that for 13X.

For a given adsorbent, the overall mass transfer coefficient of toluene was higher than that of o-xylene since the molecular size of o-xylene was larger and the length was longer than toluene, therefore it became difficult to transfer through the pore.