CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalytic Isomerization Experiments

4.1.1 Batch Isomerization

The catalytic isomerization of DMN along the 2,6-triad was batch-wisely conducted in an autoclave reactor using 10 wt% 1,5-DMN and H-beta zeolite as a feed and catalyst, respectively. The product distributions from each system are shown in Figures 4.1-4.3. It should be noted that the amount of 1,5-DMN in the product is not included in the chart. 1,5-DMN is catalytically isomerized to 1,6-DMN and subsequently to 2,6-DMN to a higher extent at higher temperatures for all solvent systems. On one hand, it was found that the use of benzene and toluene as a solvent media can facilitate the isomerization to reach its equilibrium without promoting any side reactions. On the other hand, the use of EB, pDEB, p-, o- and m-xylene as a media for the isomerization seems not appropriate since these solvents cause the formation of some side products (labeled as "unknown"), particularly at high temperatures.
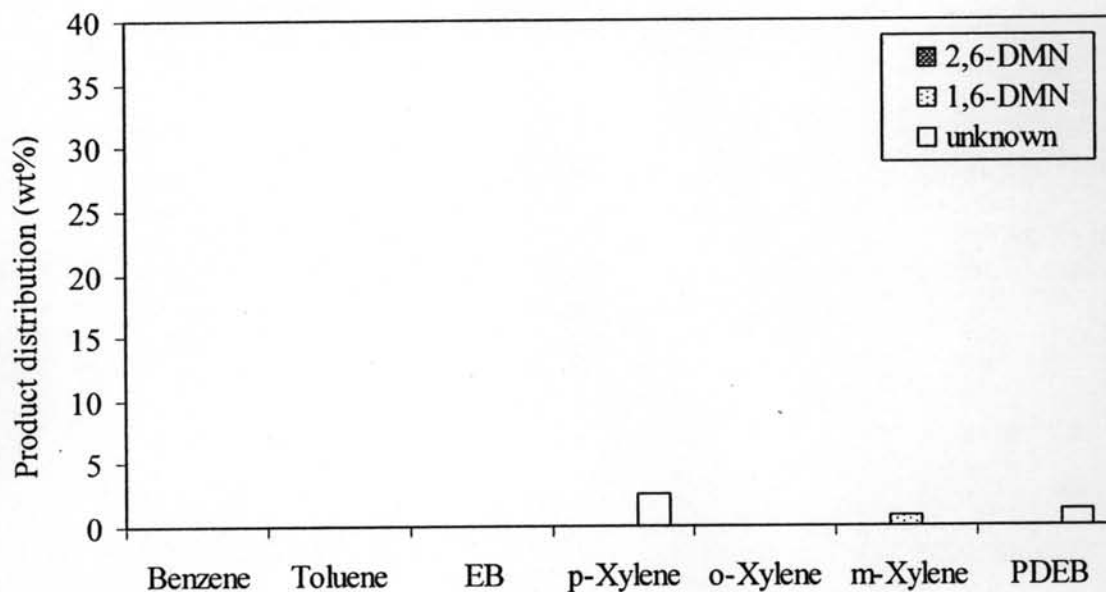
Figure 4.1 Comparisons of the catalytic isomerization of 10 wt% 1,5-DMN with H-beta zeolite in different solvents at 180°C.
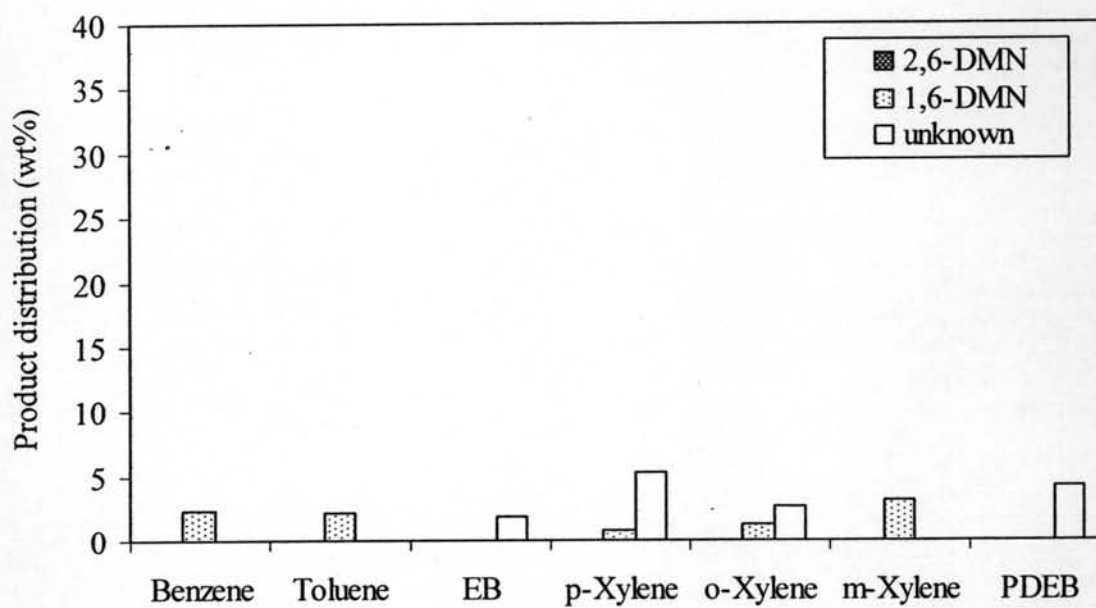

Figure 4.2 Comparisons of the catalytic isomerization of 10 wt% 1,5-DMN with H-beta zeolite in different solvents at 190°C.
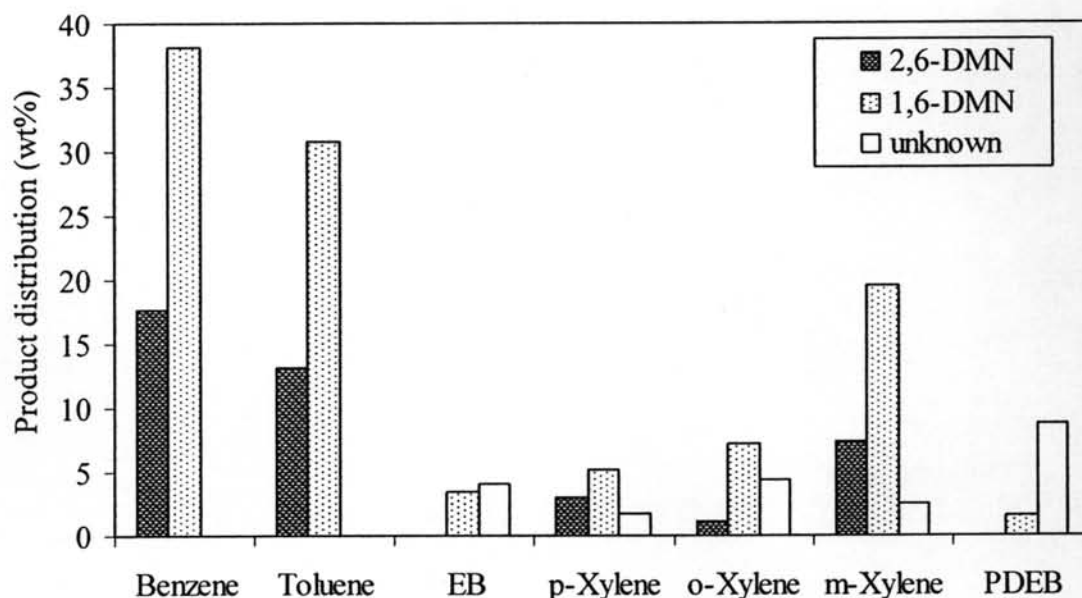
Figure 4.3 Comparisons of the catalytic isomerization of 10 wt% 1,5-DMN with H-beta zeolite in different solvents at 220°C.

From Figure 4.1, the isomerization from 1,5-DMN to 1,6-DMN can be observed only in the m-xylene system, while the side reactions are found in the p-xylene and pDEB systems. Even though the benzene and toluene systems yield no isomerization at 180°C, a small amount of 1,5-DMN was isomerized at 190°C (Figure 4.2). The p- and o-xylene systems also show the 1,5-DMN isomerization at 190°C; however, there are side reactions. Since m-xylene is the only solvent that yielded 1,6-DMN at 180°C, it was firstly expected as the most suitable solvent for the isomerization. However, there are side reactions with the isomerization when the temperature is increased. So, besides the effect of the solvents that can facilitate the reaction, their ability to control the side reactions should be considered. At 220°C, the result in Figure 4.3 indicates that 1,5-DMN was isomerized in all tested solvent systems but to different degrees. The amount of 2,6-DMN decreases in the order of the benzene > toluene > m-xylene > p-xylene > o-xylene systems.

From the result, the high extent of isomerization in the benzene, toluene, and m-xylene systems is clearly observed. For the latter two, the influence of the solvation energy, as discussed by Kraikul *et al.* (2006a), may be used to

explain the high extent. The dipole moments of the two solvents are close to that of 1,6-DMN compared with the other solvents as seen in Table 4.1. The close dipole moments contribute strong interaction between 1,6-DMN and the solvents. That interaction, therefore releases the solvation energy that reduces the thermal energy required for the first isomerization. Therefore, the amounts of 1,6- and 2,6-DMN are higher in these systems than the others. On the other hand, as benzene also yields a high amount of 2,6-DMN, there should be other parameters involved in the reaction. Since there is no side reaction in the benzene system, the isomerization proceeds without having to compete with other reactions resulting in the high amount of 2,6-DMN.

Table 4.1 Dipole moments of the solvents and DMNs (Yaws, 1999)

Solvents	Dipole moment (debye)	DMNs	Dipole moment (debye)
benzene	0	1,5-DMN	0.07
p-xylene	0	1,6-DMN	0.32
pDEB	0	2,6-DMN	0.14
m-xylene	0.33		
toluene	0.375		
EB	0.59		
o-xylene	0.62		

The side reactions may affect the isomerization by obstructing the active sites of the catalyst. Then, instead of increasing the yield of 2,6-DMN, the thermal energy is used undesirably for the side reactions. There are many side reactions that proceed from naphthalene along with the 2,6-triad isomerization, such as disproportionation and inter-triad isomerization (ChemSystems, 2000). However, the GC test suggests other side reactions. All unknowns belong to alkyl-substituted benzene compounds so they were not from 1,5-DMN. In other words, the solvents may act as another competitive reactant to the isomerization. Since there is no side reaction in the benzene and toluene systems, the side reactions occurring in the other

solvent systems are hypothesized to relate to the alkyl-substituted group of the solvents. The dealkylation at the alkyl branch of the solvent probably breaks the solvent alkyl branch to shorter ones. The longer the chain, the easier it is to accelerate the dealkylation.

To investigate the side reaction source, the autoclave experiments were re-conducted for all systems using each pure solvent as a feed at 200 and 220°C. The products from each aromatic were analyzed for their compositions and are shown in Table 4.2. Some aromatics that respond to the detector similarly to others are all reported as possible components. This result substantiates the hypothesis that the solvents are competitive reactants to the isomerization. Surprisingly, not only the dealkylation of these active solvents occurs but also other reactions that need to be further analyzed.

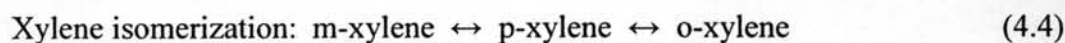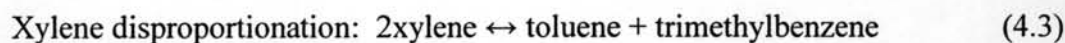**Table 4.2** Product composition from the reactions of the pure solvents with H-beta zeolite at 200 and 220°C

Solvents	Product compositions
EB	benzene, pDEB
p-xylene	toluene, m-xylene, 1,3,5-trimethylbenzene (TMB)
o-xylene	toluene, p-xylene, m-xylene, TMB
m-xylene	benzene, toluene, p-xylene, o-xylene
pDEB	toluene, EB, o-xylene, p-ethyltoluene (ET), TMB, tetramethylbenzene (TeMB), unknowns

The reaction from the EB solvent is suggested to be the disproportionation of EB to benzene and pDEB. In fact, Cejka and Wichterlova (2002) discussed that the disproportionation of EB proceeds in two steps. The first one is the disproportionation, Equation 4.1, and followed by the isomerization of pDEB to meta-diethylbenzene (mDEB), Equation 4.2. The first disproportionation step is catalyzed in the interior of the zeolite crystal. The second DEB isomerization step also occurs in the interior; however, with diffusion limitation (Arsenova-Hartel *et. al*, 2000). Since no mDEB was detected in this experiment, it may be anticipated

that the reaction is limited by mass transportation. If the reaction were prolonged, mDEB might be formed.

EB disproportionation: 2EB ↔ Benzene + pDEB   (4.1)

DEB isomerization: pDEB ↔ mDEB   (4.2)
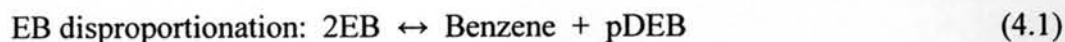
For xylene isomers, the reactions are proposed to be the isomerization, Equation 4.3, and disproportionation, Equation 4.4, in competition. No direct ortho ↔ para isomerization was found. Therefore, it suggests that only the monomolecular isomerization pathway proceeds with the same isomerization mechanism as what was suggested by Guisnet *et al.* (2000); Jones *et al.* (1999), and Perez-Pariente *et al.* (1991). The isomerization of xylenes, especially at low conversion, on the H-beta zeolite occur via the monomolecular mechanism or the intramolecular mechanism. This is due to the tortuous pore system of the zeolite, so it prefers the monomolecular pathway.
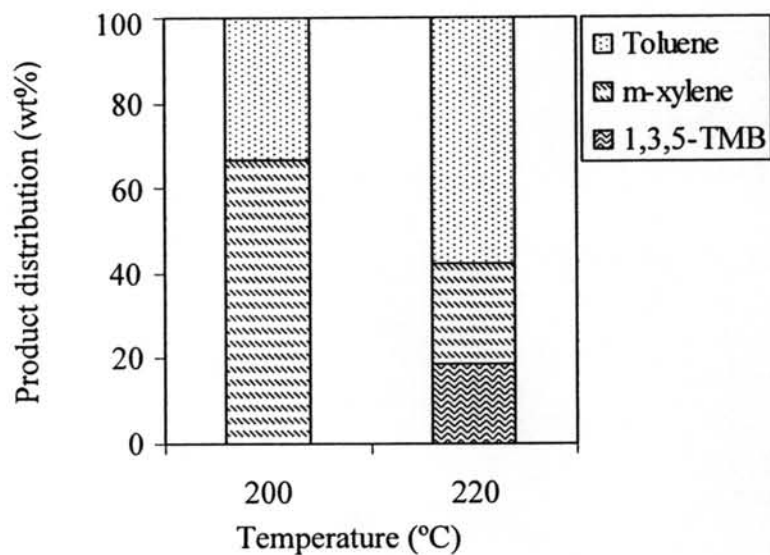
Xylene disproportionation: 2xylene ↔ toluene + trimethylbenzene   (4.3)

Xylene isomerization: m-xylene ↔ p-xylene ↔ o-xylene   (4.4)

Figure 4.4 Product distribution from the reactions of p-xylene with H-beta zeolite at 200 and 220°C.
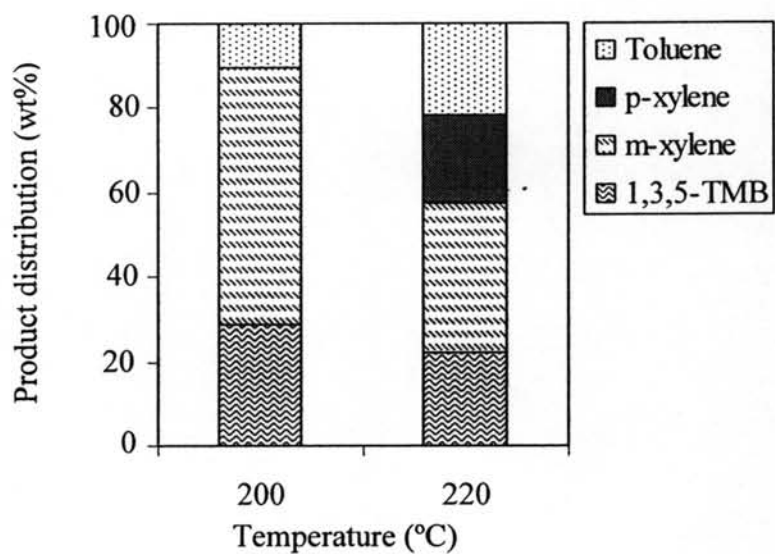

Figure 4.5 Product distribution from the reactions of o-xylene with H-beta zeolite at 200 and 220°C.
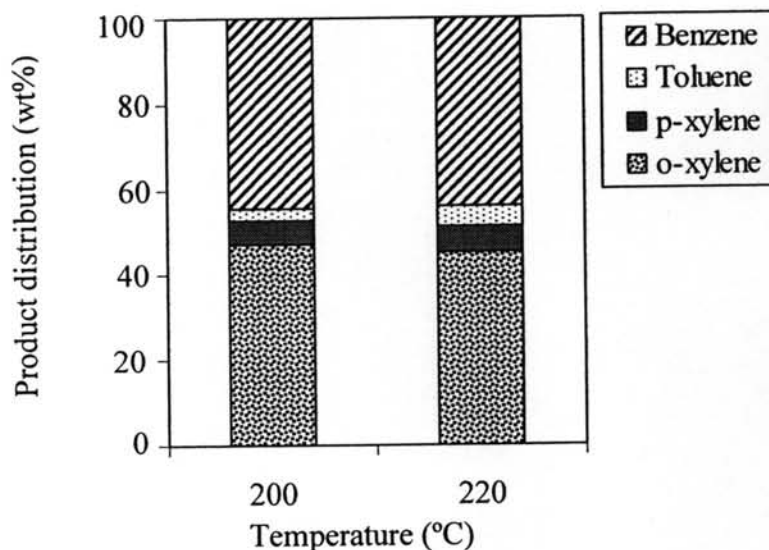
Figure 4.6 Product distribution from the reactions of m-xylene with H-beta zeolite at 200 and 220°C.

From Figures 4.4-4.6, we can see that the isomerization of xylenes seems to be dominant at low temperature. Then, as the temperature increases, the disproportionation is enhanced due to the higher thermal energy for the diffusion of the reaction product, TMB, through the zeolite pore. However, there is no TMB and little toluene detected in the product from m-xylene. This may possibly be due to two reactions; the isomerization of m-xylene and toluene disproportionation. The first one is likely because of a bulky molecule of TMB in the zeolite framework. The molecule has to be dealkylated into smaller ones such as benzene. In the second reaction, toluene breaks down into benzene and xylene.

For pDEB, the possible reactions are dealkylation of the aromatic to small aromatics; that is, toluene, EB, o-xylene, ET and TMB. No isomerization among DEB is observed, since there are no other DEB isomers. Besides the dealkylation, there is a transformation of pDEB into TeMB. The ET disproportionation or the reverse transalkylation between DEB may also occur. The product distribution shown in Figure 4.7 is not much different between the two testing temperatures except for the formation of o-xylene and 1,2,3,4-TeMB as the

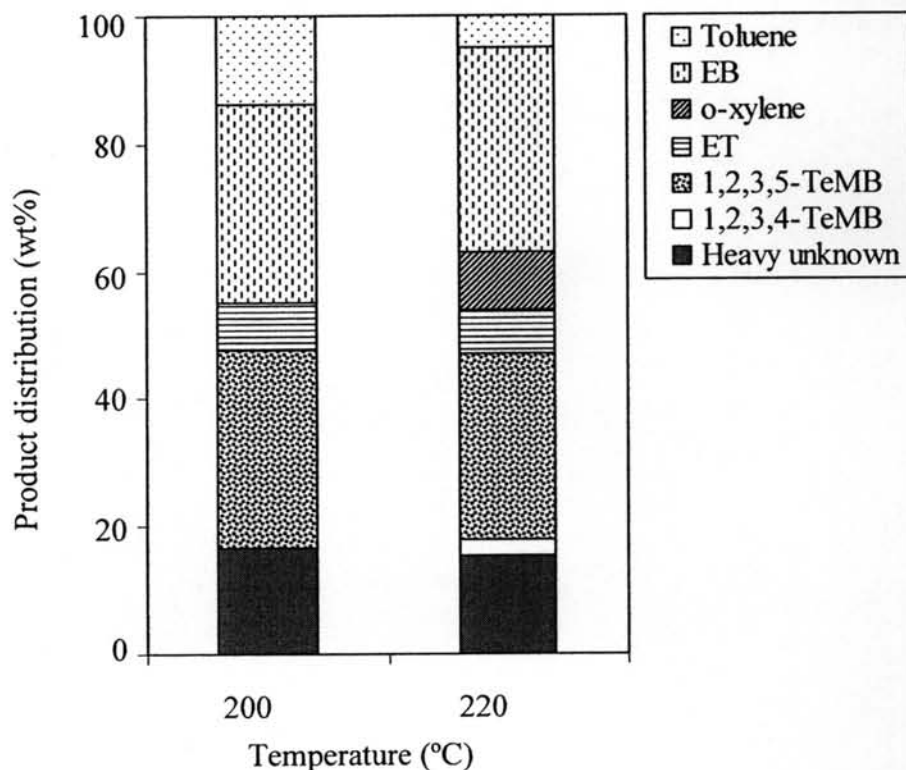temperature is increased. The smaller percentage of toluene is observed along with the occurrence of o-xylene.

Figure 4.7 Product distribution from the reactions of pDEB with H-beta zeolite at 200 and 220°C.

In order to investigate the temperature effect, the amount of products produced from each solvent is compared and illustrated in Figure 4.8. The chart clearly indicates that benzene and toluene act as inert solvents under the studied temperatures. The other solvents provide about 0.2-6 wt% of product. In contrast, the reaction from some solvents is observed as a strong function of temperature. For example, EB that has no side products at 200°C, but a considerable amount can be observed at 220°C. All in all, the use of m-xylene creates the highest amount of products; thus, it is considered to be the most active solvent over H-beta zeolite in this study.

We believe that the reactivity of the solvents would somewhat result from two reasons; acid-base interaction and molecular diffusion. It is known that an aromatic can show its basic characteristic under acid conditions. Therefore, by employing the acid H-beta zeolite, the basicity of the solvents in our study results in different reactivity toward the acid zeolite. In this research, the basicity is defined as shown in Appendix B. Figure 4.8 gives the correlation between the basicity and the amount of products, from the reactions of each solvent at 200 and 220°C. The activity of the solvent increases with the basic properties as predicted. However, toluene and EB have a considerably different amount of the products even with almost the same basicity. Furthermore, although the basicity of p- and o-xylene increases, the amounts of the products are lower than that of pDEB. This indicates, therefore, that there are other parameters controlling the reactions of the solvents.

Because there is no product from toluene and only a small amount from p-xylene, it may be suggested that the diffusion ability be a parameter limiting the reaction. As the kinetic diameters of toluene and p-xylene (5.8 Å) are smaller than the other solvents, these two solvents would easily diffuse through the zeolite pore and result in low interaction with the zeolite acid surface. On the other hand, larger aromatics, o- and m-xylene (6.8 Å), also have acid-base interaction due to their high basicity along the diffusion. Their activity with the zeolite is therefore higher. For pDEB, because of its bulky structure, the steric hindrance possibly limits its diffusion, and then the reaction.
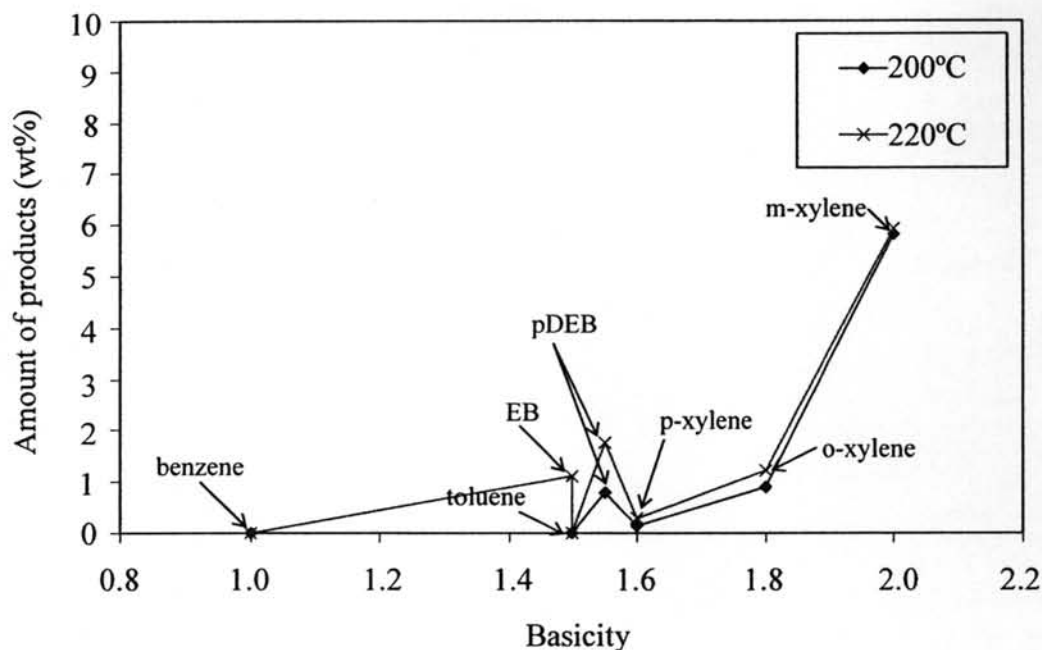
Figures 4.8 Relationship between amount of products at 200 and 220°C and basicity of different solvents in the H-beta zeolite catalyst.

If m-xylene is used as a solvent for 1,5-DMN, the highest amount of unknown due to the reactions of m-xylene itself on the catalyst should be expected. However, when the amount of unknown produced from 10 wt% 1,5-DMN in different solvents at 220°C is compared, in Figure 4.9, the result indicates otherwise. It suggests different activity of the solvents with the amount of 1,5-DMN in the feed. From the figure, it can be seen that all solvents except m-xylene have a higher amount of products in the presence of 1,5-DMN. In other words, the solvents enhance the side reactions if 1,5-DMN is present in the system. On the contrary, m-xylene, which is very reactive over the catalyst in the pure solvent system, can somehow facilitate the 1,5-DMN isomerization. Therefore, the result suggests the effect of the interaction due to the dissolving of 1,5-DMN on the solvent activity over the catalyst.
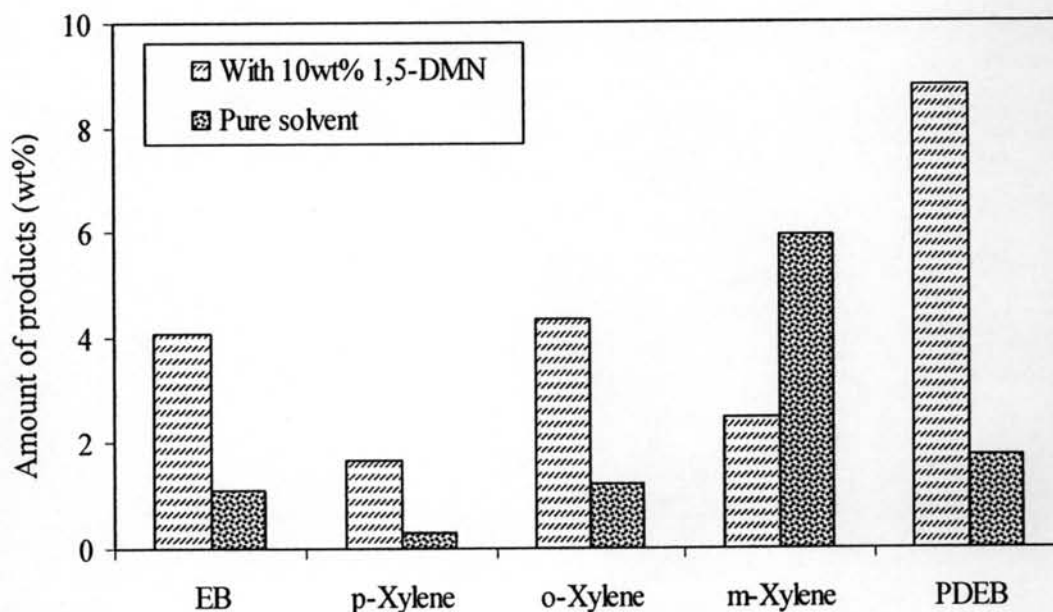
Figures 4.9 Amount of products obtained at 220°C from different solvents in the H-beta zeolite catalyst.

In any case, the above result confirms that the use of these active solvents leads to a competitive catalytic expediting of the isomerization of DMNs along the 2,6-triad under the studied conditions. 1,5-DMN should be dissolved in an inert solvent that can suppress the side reactions. Then, only benzene and toluene were selected to study their effects on the 2,6-triad isomerization in a continuous flow system.

4.1.2 Continuous Isomerization

The isomerization in the continuous mode was studied in the temperature range of 180-240°C at 30 h^{-1} LHSV and 10 wt% 1,5-DMN. The product distribution in the system with toluene along with results from Kraikul *et al.* (2006a) and Kraikul *et al.* (2005) are illustrated in Figures 4.10 and 4.11, respectively.
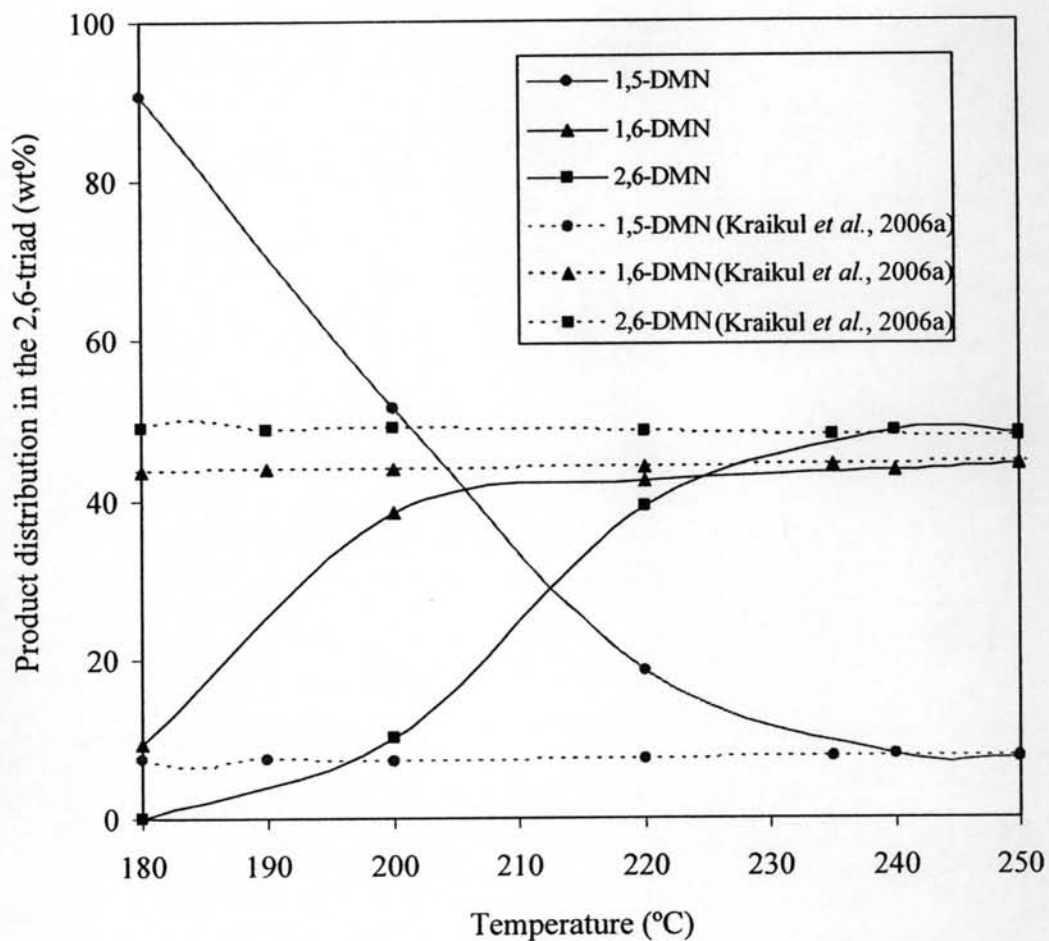
Figure 4.10 Product distribution profiles from the catalytic isomerization of 10 wt% 1,5-DMN at 30 h^{-1} LHSV with the H-beta catalyst and toluene solvent as a function of temperature compared with Kraikul *et al.* (2006a) (30 h^{-1} LHSV and 10 wt% 1,5-DMN).
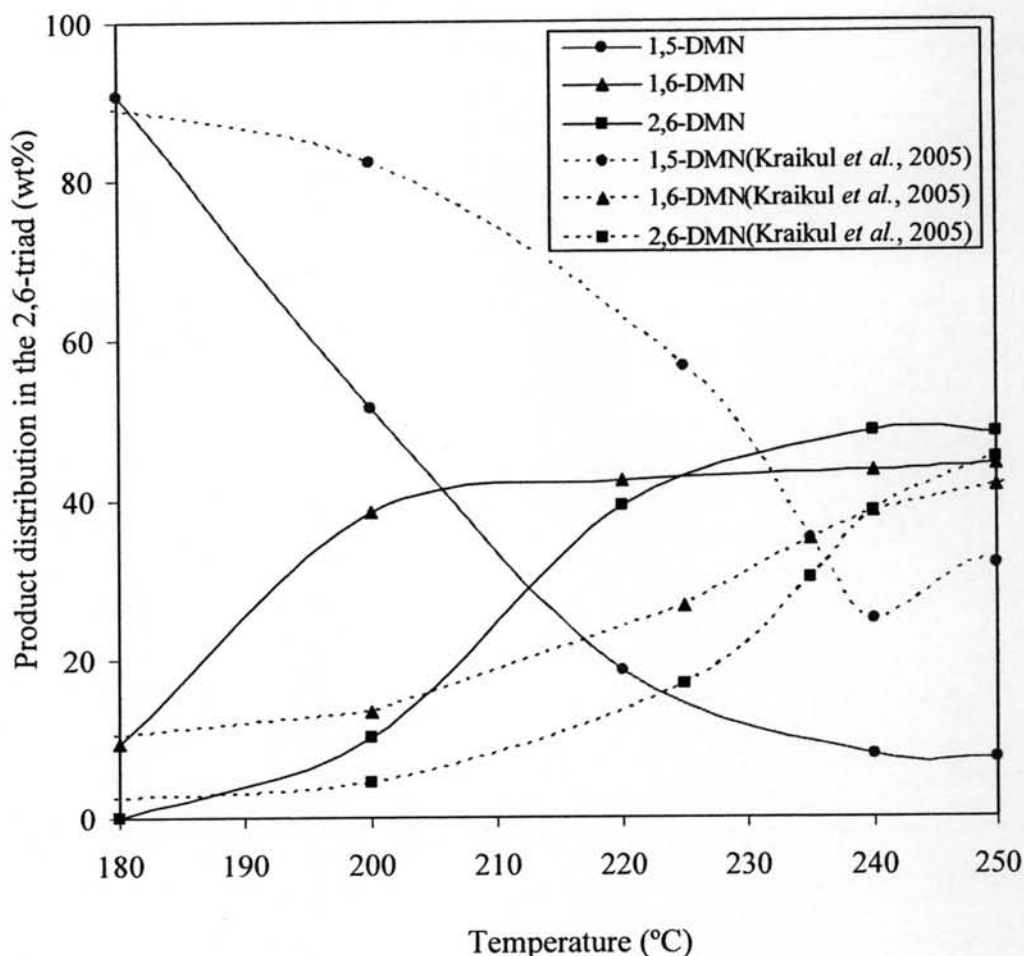
Figure 4.11 Product distribution profiles from the catalytic isomerization of 10 wt% 1,5-DMN at 30 h⁻¹ LHSV with the H-beta catalyst and toluene solvent as a function of temperature compared with Kraikul *et al.* (2005) (Solvent-free isomerization, a batch reactor with 3 wt% H-beta catalyst, 1 hour reaction time).

From Figure 4.10, we can see that the isomerization reaches its equilibrium with 48 wt% 2,6-DMN after the temperature is higher than 240°C. Hence, the system is thermodynamically controlled at this temperature, as discussed in Kraikul *et al.* (2006a). However, differences between our experiment and that of Kraikul *et al.* (2006a) at a temperature lower than 240°C are clearly observed. Much higher thermal energy is required to drive the reaction, and the isomerization strongly depends on the temperature. In addition, the result at 180°C is close to the solvent-

free isomerization in a batch reactor (Figure 4.11). The conversion of 1,5-DMN is only 10 wt% and none of the second isomerization can be observed. It is at a temperature higher than 180°C that the isomerization proceeds at a considerable extent in the continuous system. Therefore, the result indicates that the isomerization is more kinetic-controlled in our experiment than in Kraikul *et al.* (2006a). The exact reason for this different result is not clear, so further investigation is needed.

Moreover, there are no side reactions in the continuous system so the selectivity toward the 2,6-triad isomerization in our experiment is 100%. This is also different from Kraikul *et al.* (2006a) where the by-products can be observed at only 190°C. It was suggested in his work that the energy applied to the system is firstly consumed by the isomerization in the 2,6-triad before the excess is utilized by other side reactions. Since higher thermal energy is needed in our system, it may cause a lack of thermal energy for the side reactions. Then, no side reaction is observed.

A comparison plot between product distributions from 1,5-DMN isomerization with H-beta zeolite at different temperatures in toluene and benzene is shown in Figure 4.12. The use of benzene still maintains 100% selectivity toward the 2,6-triad. However, the result shows a considerably different performance between the two media, although rarely any difference is observed in the batch isomerization experiment (Figure 4.3). It can be observed that the degree of isomerization in the benzene system is less than that in the toluene system, especially at 200°C. Moreover, the isomerization in benzene is unable to reach its thermodynamic equilibrium, even at a temperature as high as 240°C.
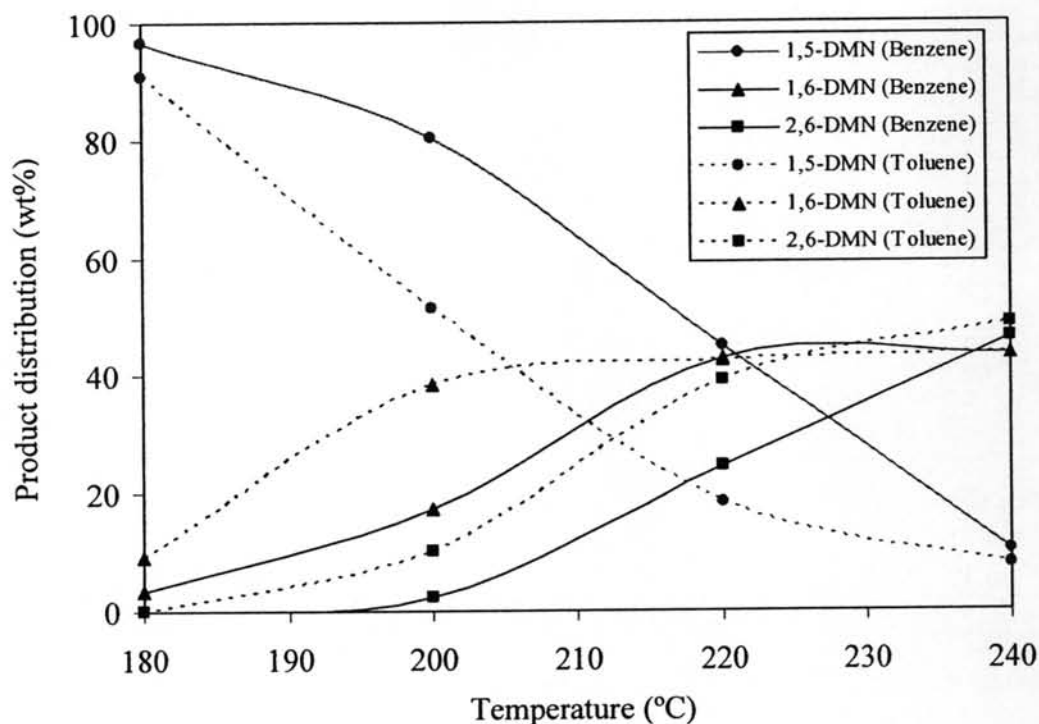
Figure 4.12 Product distribution profiles from the catalytic isomerization of 10 wt% 1,5-DMN at 30 h^{-1} LHSV with the H-beta catalyst as a function of temperature obtained from the toluene and benzene systems.

Furthermore, the equilibrium constants of the 1st and 2nd isomerization step, $K_{1,5-1,6}$ and $K_{1,6-2,6}$, respectively, were calculated and plotted with the temperature (see Figure 4.13). The constants depend strongly on the temperature, particularly $K_{1,5-1,6}$ for both solvents. A decrease in the equilibrium constant is clearly observed with the change from toluene to benzene, except $K_{1,6-2,6}$ at 240°C where the reaction approaches to its equilibrium.

It is suggested that the factor controlling the isomerization with a solvent is the interaction between DMNs and the solvent media (Kraikul *et al.*, 2006a). A non-dipole molecule like benzene truly has less interaction than the dipole toluene molecule (0.36D). The close dipole moment between 1,6-DMN (0.32D) and toluene improves the first isomerization that limits the overall reaction. The dipole moment of benzene is close to that of 1,5-DMN (0.05D). Possibly, this explains why

benzene does not facilitate the reaction as well as toluene. Therefore, further study is needed to find the most suitable solvent that can facilitate 1,5-DMN isomerization.
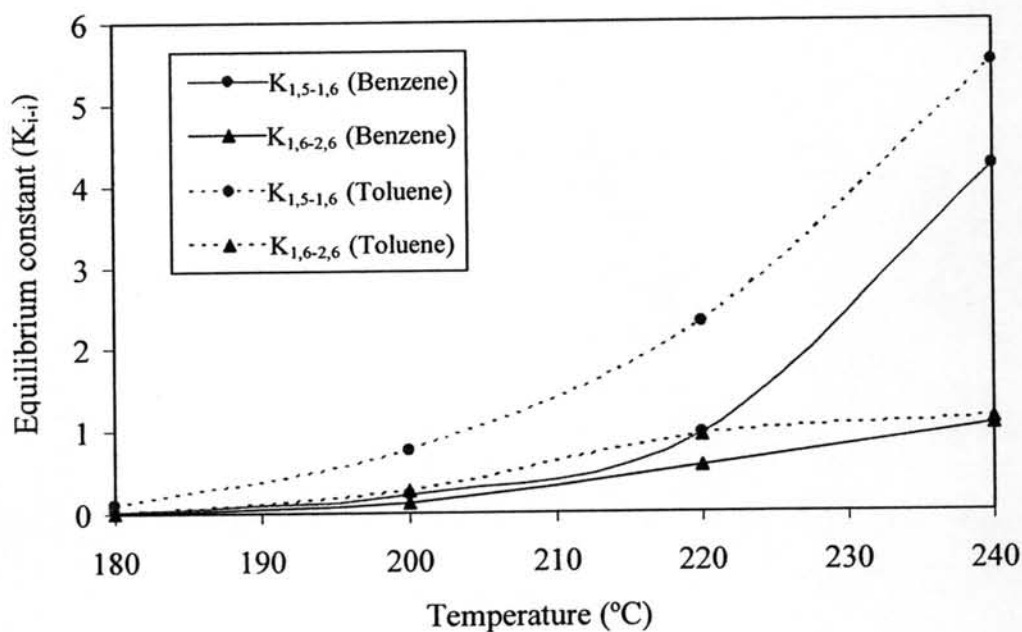

Figure 4.13 Equilibrium constants, K_{i-j}, as a function of temperature obtained from the toluene system compared with the benzene system.

4.2 Dynamic Adsorption Experiments

4.2.1 NaY Adsorbent

The adsorption of the 2,6-triad DMN isomers was carried out over the NaY adsorbent ($Si/Al_2 = 5.0$). Seven solvents were now used as desorbents for the separation with n-nonane as a tracer. The elution profiles of 1,5-, 1,6- and 2,6-DMN are given in Figure 4.14. It can be seen that the adsorption and desorption of DMN isomers are a function of desorbent. With benzene and m-xylene desorbents, DMNs elute at the same time with the tracer. Moreover, the narrow DMN peaks also indicate a high rate of desorption. The result shows that the adsorption of DMNs onto the adsorbent surface is strongly diminished. In other words, the interaction of the DMNs with the adsorbent is so weak that the desorption can easily take place. This

suggests the importance of the balance between the adsorptivity of DMNs and desorbent, as discussed in Morbidelli *et al.* (1995) and Kulprathipanja (1998). For this case, the adsorption of benzene and m-xylene are stronger than that of DMNs. It seems that they are not suitable to separate 2,6-DMN from the other isomers.

For most systems, the net retention volume (NRV) magnitude follows the order of 1,5-DMN > 1,6-DMN > 2,6-DMN. The high affinity of 1,5-DMN results in the desorption difficulty. The wide 1,5-DMN peak indicates a low rate of exchange between the DMN and the desorbent while 2,6-DMN behaves in the opposite way. As a result, the separation of 2,6-DMN can be accomplished only in a rejective system, as discussed by Kraikul *et al.* (2006b). Even though being the rejective isomer, 2,6-DMN reveals some interaction with the adsorbent in the EB and pDEB systems. It can be postulated that the adsorption of the desorbents is weak enough to enable the competitive adsorption of 2,6-DMN. In other words, the desorbents allow the isomer to diffuse into the zeolite pore and interact with the zeolite. Although the adsorption of 2,6-DMN is achieved only in the rejective system, a separated peak of 2,6-DMN in the EB and pDEB systems suggests a possibility of 2,6-DMN purification from its equilibrium mixture. The best separation among the three DMNs is observed with the pDEB system. It suggests that the balance between the adsorbent-adsorbates and adsorbent-desorbent interactions would be the best among all desorbents. Although the EB system accomplishes 2,6-DMN separation, it does not give good 1,5-DMN and 1,6-DMN separation.

In the toluene system, a difference in the selectivity between 1,5-DMN and 1,6-DMN can be observed. This suggests the specific interaction between toluene and the adsorbent. Then, it results in the desorption of 1,5-DMN instead of 1,6-DMN as found with the separation of C_8 aromatics by using benzene as a desorbent (Barthomeuf, 1996).
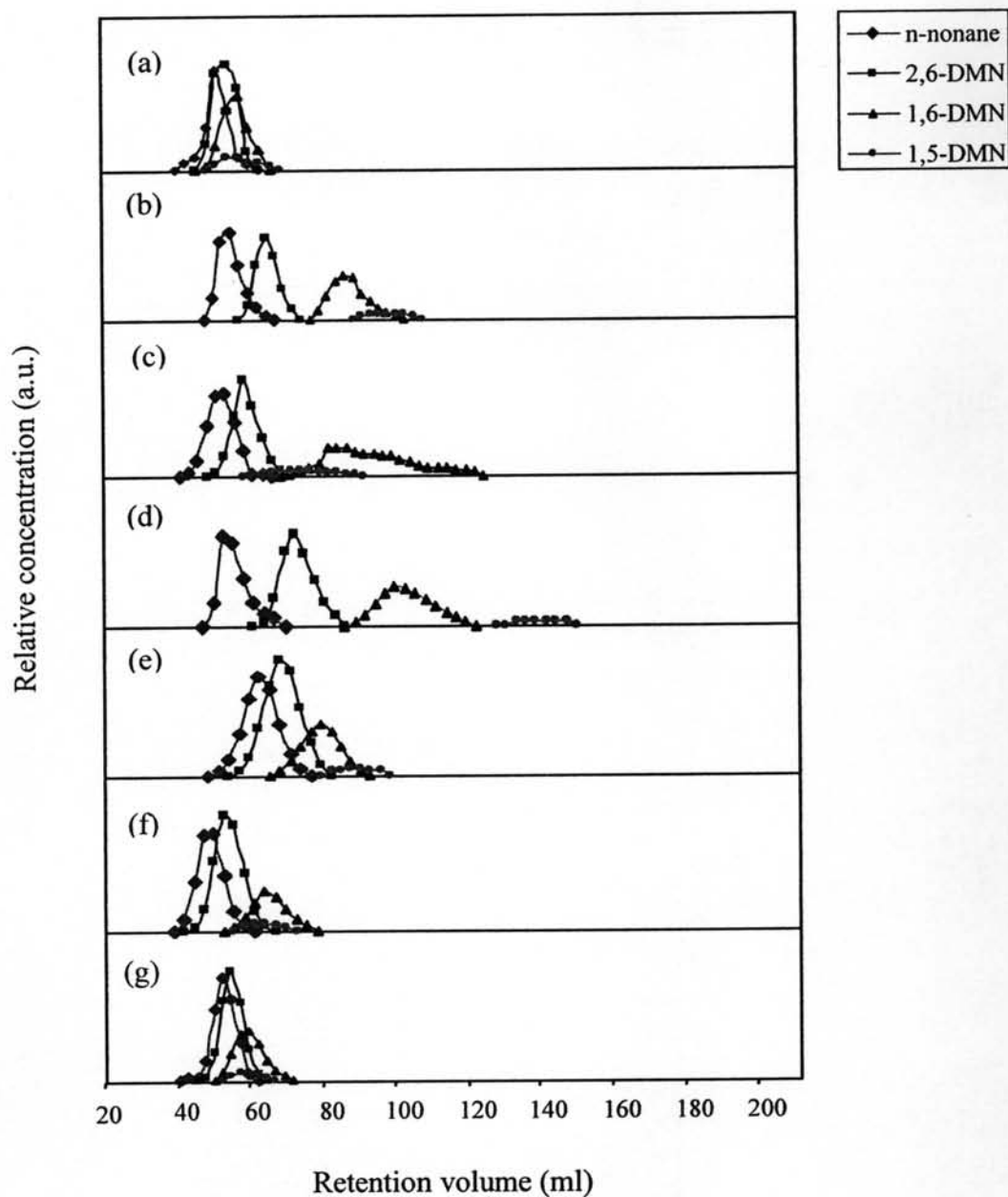
Figure 4.14 Elution profile of 1,5-, 1,6-, and 2,6-DMN on NaY at 1 h^{-1} LHSV, 180°C from different desorbents: (a) benzene, (b) EB, (c) toluene, (d) pDEB, (e) p-xylene, (f) o-xylene, and (g) m-xylene.

Under acidic and basic adsorption sites in the FAU zeolite structure, the adsorption is believed to proceed via the specific interactions of ¶ electrons with cations and CH with oxygens framework (Barthomeuf, 1996). The location of one

aromatic in the zeolite depends on the balance between the adsorption on each site. In other words, the acidobasicity of an adsorbent determines the adsorptivity of an aromatic. In order to investigate the different behaviors of the desorbents used in our experiments, the correlation between the desorbents' basicity and the NRVs was made and is shown in Figure 4.15. If the desorption is controlled by the acid-base interaction, the high basicity of a desorbent should show better desorption or a lower NRV. Nevertheless, the result shows otherwise. In general, as the basicity increases; the NRVs of DMNs increase to a certain extent. The maximum NRV is obtained with pDEB and decreases afterwards. Therefore, it can be interpreted that the desorption would not be dominated solely by the acid-base interaction, but only partially controlled.
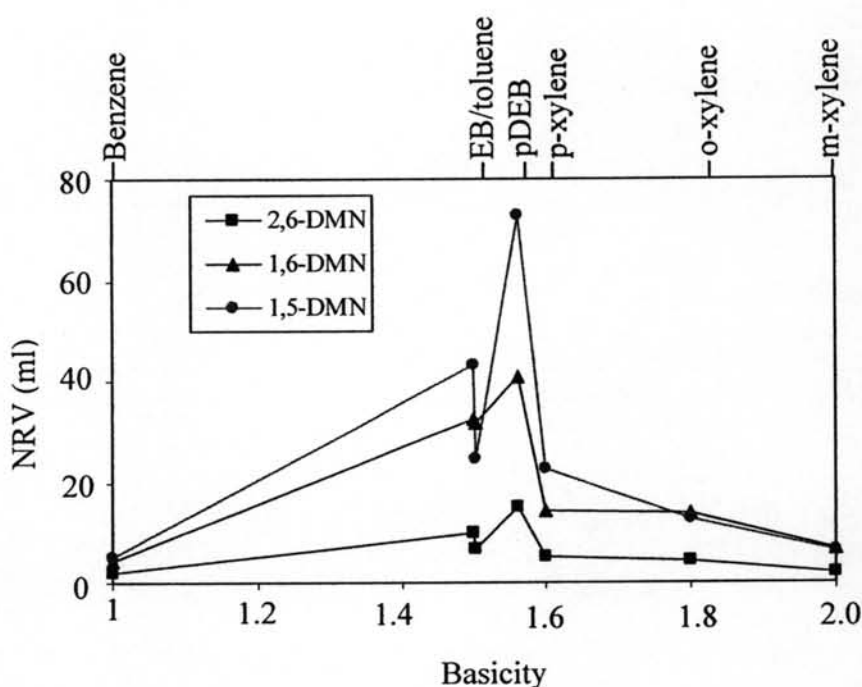

Figure 4.15 Correlation plot between basicity of different desorbents and the NRV of DMNs on NaY.

From Figure 4.15, by changing from p-xylene to o-xylene, the adsorption of 2,6-DMN and 1,6-DMN does not show any difference while the NRV of 1,5-DMN is reduced to about that of 1,6-DMN. The highest basicity desorbent, m-

xylene, decreases the NRVs of 1,5- and 1,6-DMN to be close to that of 2,6-DMN as well as sharpening the elution peak of the three isomers. m-Xylene is found to be the most preferentially adsorbed of the four C_8 aromatics toward NaY zeolite because of its highest basicity (Barthomeuf and De Mallmann, 1990). Therefore, its interaction with NaY provides strong desorption of DMNs, as shown in our result.

For pDEB, its lower basicity than those of xylenes provides higher NRVs for the three isomers. However, the decrease in the NRVs from pDEB desorbent to p-xylene is obviously not in the same trend as the decrease in the NRVs among the xylenes. In other words, the result reveals other parameters affecting the desorption besides the acid-base interaction. Moreover, it can be postulated that probably the acid-base interaction would dominate if high basicity desorbents are employed. In our study, these desorbents are the xylenes, while benzene, EB, toluene and pDEB desorbents have too low basicity.

We believe that the pDEB desorption is dominated by the molecular structure, i.e. diethyl substituted group. Its bulky structure creates the steric hindrance and deters its interaction not only with the zeolite but also with the DMNs. Therefore, we hypothesize that the structure of a desorbent plays an important role in the desorption. In order to substantiate the effect from the desorbent structure, the plot in Figure 4.16 was created to compare the effect from the number of carbons in the alkyl branch chain of the aromatics.
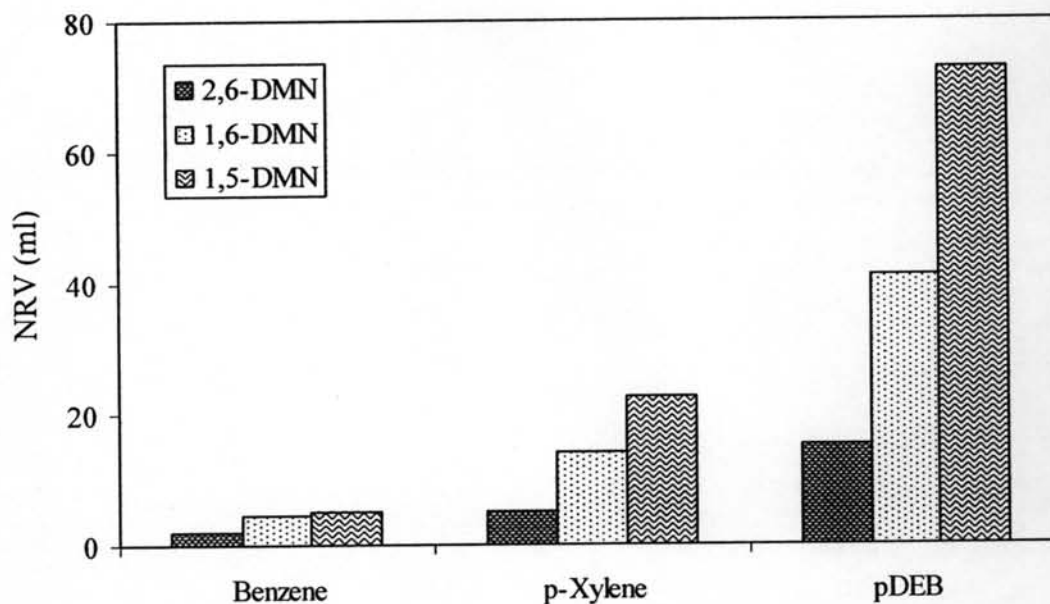
Figure 4.16 NRVs of 1,5-, 1,6-, and 2,6-DMN on NaY with benzene, p-xylene, and pDEB desorbents.

As the number of carbons in the para-substituted alkyl chain increases, the tendency of the NRVs evidently increases. As a result, the longer the alkyl chain is, the harder the diffusion should be. For pDEB, while it removes DMNs from the zeolite surface, it does not easily diffuse into the zeolite pore, and then results in high NRVs. So, the result indicates that the desorption be controlled by the rate-selective mechanism. Consequently, if two desorbents have the same diffusion parameter, i.e. kinetic diameter, the NRVs from these two systems should be comparable. However, when the NRVs from benzene, toluene, and p-xylene desorbents having the same kinetic diameter are compared in Figure 4.17, the result reveals otherwise.
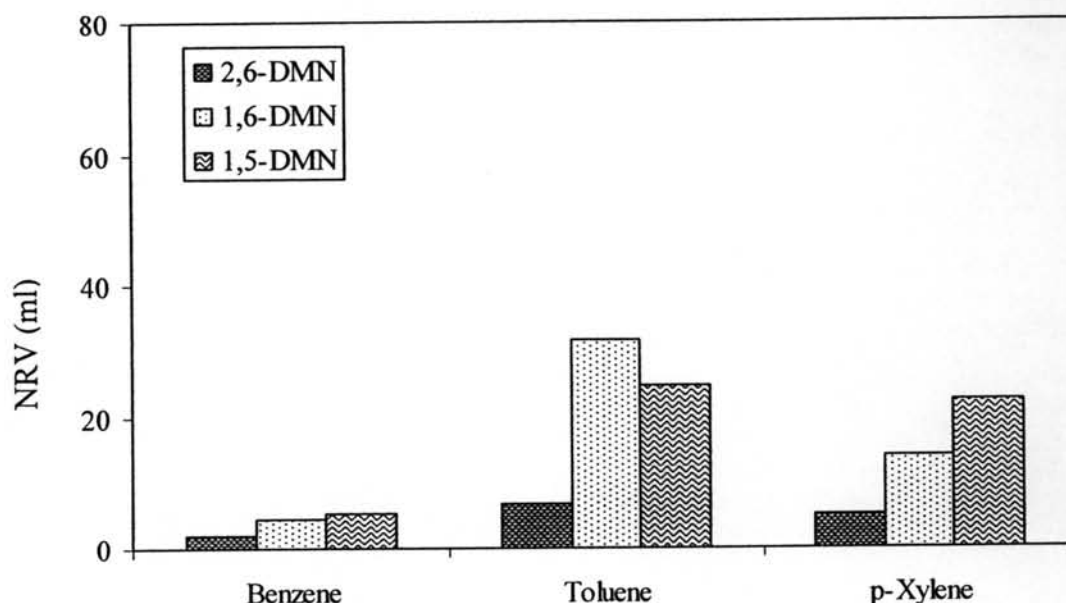
Figure 4.17 NRVs of 1,5-, 1,6-, and 2,6-DMN on NaY with benzene, toluene, and p-xylene desorbents.

From Figure 4.17, although these three desorbents have the same kinetic diameter, the desorption does not show the same behavior. Therefore, it can be concluded that the rate selective mechanism is not the only controlling parameter among our employed desorbents. As discussed beforehand, toluene provides strong modification of NaY to preferentially adsorb 1,6-DMN instead of 1,5-DMN. So, there should be a competitive adsorption between toluene and 1,6-DMN. However, the parameter that causes toluene to interact closely to 1,6-DMN is still not well understood, but it is believed to be due to the specific interaction between toluene and NaY. It is this interaction that diminishes the effect from the diffusion. Since the interaction strongly attaches the desorbent with the zeolite, that interaction then becomes the controlling factor to the separation.

Another effect that should be considered is that from the dipole moment. The dipole-dipole interaction involves not only between the desorbent and the zeolite, but also between the desorbent and DMNs. An investigation for the effect of the interaction of the desorbents was done through the correlation plot between the desorbents' dipole moments and the NRVs in Figure 4.18. It should be noted that

benzene, p-xylene, and pDEB are not included in the plot since they are non-dipole moment compounds.
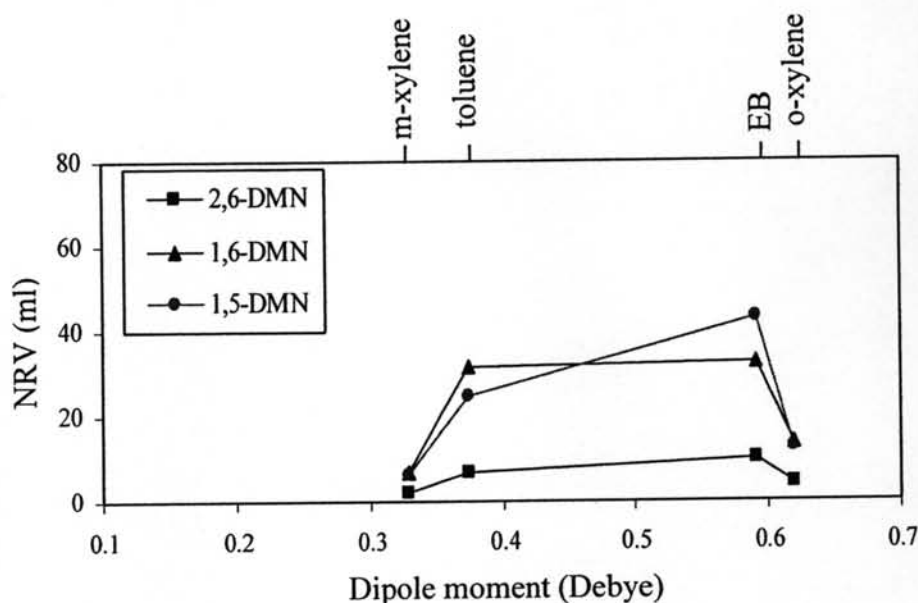

Figure 4.18 Correlation plot of the dipole moment from different desorbents and the NRV on NaY.

The dipole moment higher than 0.4 debye does not provide any difference in the desorption of 2,6- and 1,6-DMN, but provides a weaker desorption of 1,5-DMN. Then, after the dipole moment is further increased to 0.6 debye, the dipole-dipole interaction enhances the desorption strength, and then the NRVs reduce. Therefore, despite the close dipole moment of m-xylene-toluene and EB-o-xylene, the NRVs are not similar. The result indicates that the dipole moment does not affect the adsorption, because as NaY is normally considered as a medium polar zeolite, its dipole strength may not be comparable with other specific interactions dealing with the zeolite framework and cation. For example, the acid-base interaction is dominant between m-xylene and zeolite.

For benzene, the diminishing in the DMNs adsorption as seen in the elution profile (Figure 4.14) suggests the strong interaction of benzene in the zeolite.

It has been determined that this aromatic adsorbed on different sites from other C_8 aromatics. The adsorption site of C_8 aromatics, i.e. EB, o-, m-, p-xylene, and toluene is known to be mainly on the cation site in the 6R (Figure 4.19) (Barthomeuf, 1996). In contrast, benzene, with its small and symmetrical structure, preferentially adsorbs on the negative charge of framework oxygen atoms in the 12R window of faujusite zeolite, especially at high loading (Figure 4.20) (Barthomeuf, 1996; Daems *et al.*, 2006). The competitive adsorption between DMNs and benzene contributes toward the interaction in the 12R window. Then, the bulkier DMN molecules have weak interaction with the adsorbent. From the elution profile (Figure 4.14 (a)), it can be seen that DMNs elute almost at the same time with the tracer. Therefore, the bulky DMNs cannot compete with benzene to adsorb on the adsorbent. This implies the importance of the oxygen basic sites to the accommodation of DMNs in the FAU framework.
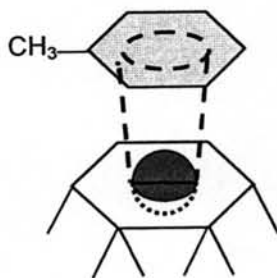

Figure 4.19 Schematic representation of ¶-electrons of toluene interacting with zeolite cation sites.

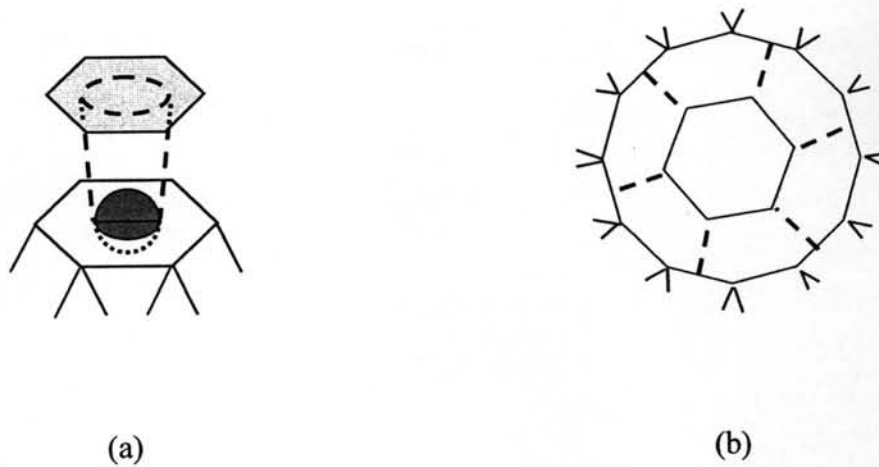(a)   (b)

Figure 4.20 Schematic representation of benzene interacting with zeolite sites: (a) ¶-electrons of benzene with cations; (b) CH of benzene interacting with oxygen atoms of a 12R window (Barthomeuf, 1996).

We already know that the balance between the adsorptivity of DMNs and desorbent is an important criteria for the adsorptive separation. There are many parameters involved in the adsortivity of the desorbents. The most basic one is the kinetic diameter that determines the rate of diffusion. However, the desorption does not proceed simply via the rate-selective mechanism. There are many interactions involved and resulting in the competitive adsorption between the desorbent and DMNs. Some are very strong and specific to some desorbents. It is impossible to consider each effect separately or to decide which effect is dominant. However, the potential for NaY as an adsorbent for 2,6-DMN purification is ensured with EB and pDEB as desorbents. Therefore, the balance between the adsorptivity of DMNs and desorbent can be achieved from these two separation systems.

4.2.2 NaX Adsorbent

The adsorption was carried out by using the NaX ($Si/Al_2 = 2.5$) adsorbent. The elution profiles of 1,5-, 1,6-, and 2,6-DMN are illustrated in Figure 4.21. In order to clearly observe its adsorption behavior, the concentration of 1,5-DMN in the EB, pDEB, toluene ,and o-xylene systems was increased from 0.8 to 5.0 wt%, so the composition of DMNs in those systems is 30 wt% 1,5-DMN, 33 wt%

1,6-DMN and 37 wt% 2,6-DMN. Since the dilution of the feed DMNs is done in the pulse test, the effect from the concentration was considered to be insignificant.

From the elution profile, the adsorption of DMNs can be observed in every system. The NRV magnitude of the DMNs still follows the order of 1,5-DMN > 1,6-DMN > 2,6-DMN. Possessing the highest affinity, 1,5-DMN is clearly separated from the other two isomers in every system. However, it seems that the adsorptivity of the desorbents is not strong enough to compete with 1,5-DMN adsorptivity. The adsorption of the isomer is too tight to be desorbed when pDEB is employed as a desorbent. Consequently, there is no elution peak of 1,5-DMN in the elution profile of the pDEB system. It should be noted that the desorption of 1,5-DMN with a benzene desorbent is not well completed in the study. Because of the very high interaction, the low desorption rate of 1,5-DMN is shown in every system, as can be observed from the broad elution shape. The desorption of the other two isomers appears to be easier due to lower adsorption affinity; however, very broad elution profiles of 1,6-DMN are shown with the benzene and pDEB systems.
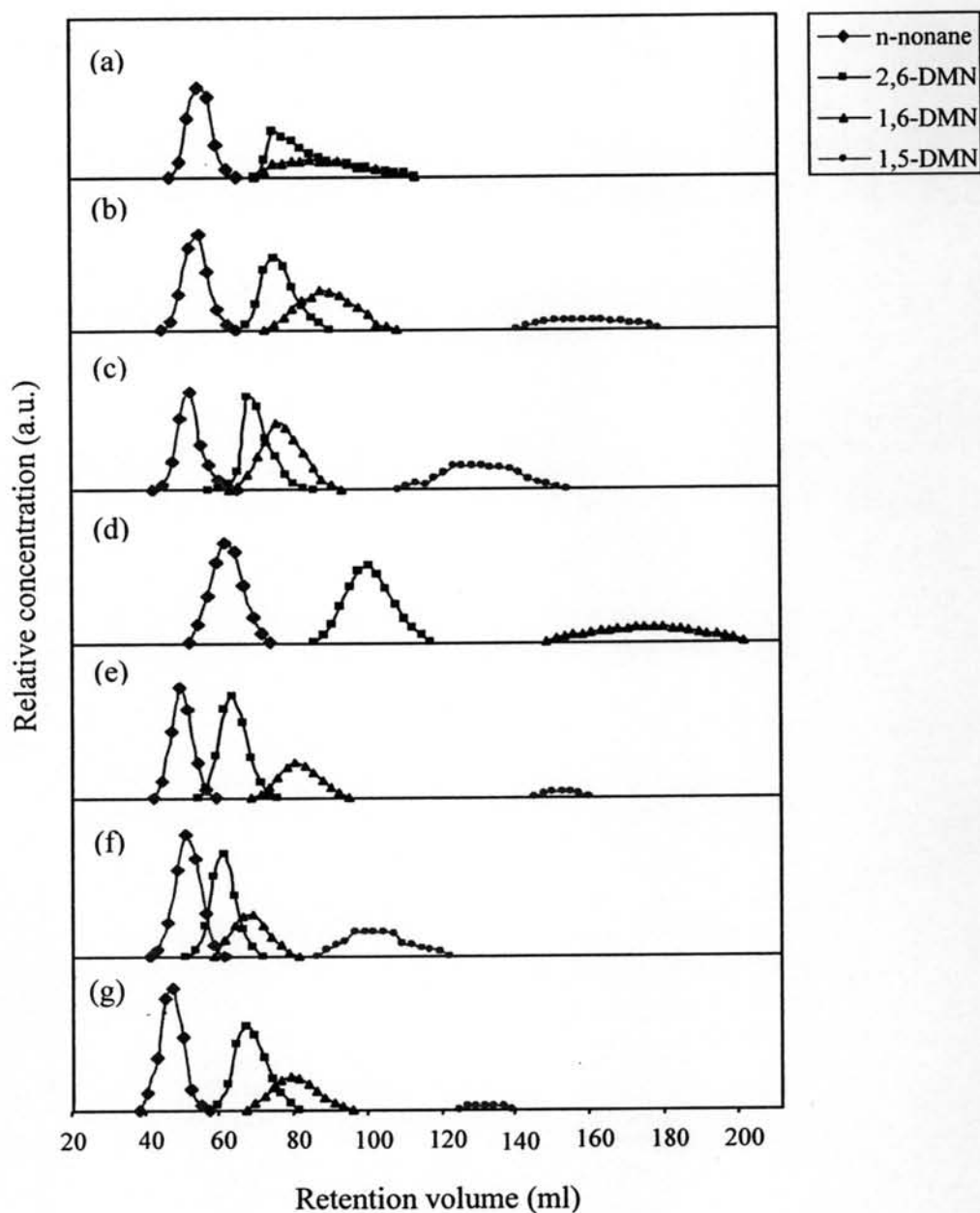
Figure 4.21 Elution profile of 1,5-, 1,6-, and 2,6-DMN on NaX at 1 h⁻¹ LHSV, 180°C from different desorbents: (a) benzene, (b) EB, (c) toluene, (d) pDEB, (e) p-xylene, (f) o-xylene, and (g) m-xylene.

Despite being the rejective component, 2,6-DMN interacts with the adsorbent in every adsorption system. That interaction is quite strong in the benzene system, as can be seen from the broad elution peak. In addition, the benzene system is incapable of separating 2,6-DMN and 1,6-DMN because the difference in their

adsorption affinities is eliminated. The EB, toluene, o-xylene, and m-xylene systems do not separate the two species, but some differences in their interactions can be observed from the partial crossing of their elution peaks. The separation between 2,6-DMN and 1,6-DMN is successfully achieved only in the pDEB and p-xylene systems.

The best separation system among the three isomers is achieved with p-xylene as the desorbent. However, it is not considerably effective from an economic point of view due to the fact that the desorption of 1,5-DMN is completed at a rather high NRV. From the above discussion, the adsorption over NaX possesses high affinities and requires a strong desorbent. The strong one is then able to separate 1,5-DMN, but may interfere in the separation of 1,6-DMN and 2,6-DMN. Therefore, adsorptive separation using NaX shows the dependency on the desorbents.

NaX is normally considered a medium acid zeolite (Bathomeuf, 1996), so it interacts strongly with a basic adsorbate, unlike in the case of NaY. The acid-base interaction on NaX appears differently. For example, o-xylene is preferentially adsorbed from the other C_8 aromatics on NaX instead of m-xylene, although it is less basic than EB (Suntornpun, 2002). If the adsorption is affected from this interaction, a strong desorption should be shown with one range of basicity of the desorbents. To show the effect from different basic properties of the desorbents, Figure 4.22 gives the correlation between the NRVs and the basicity.
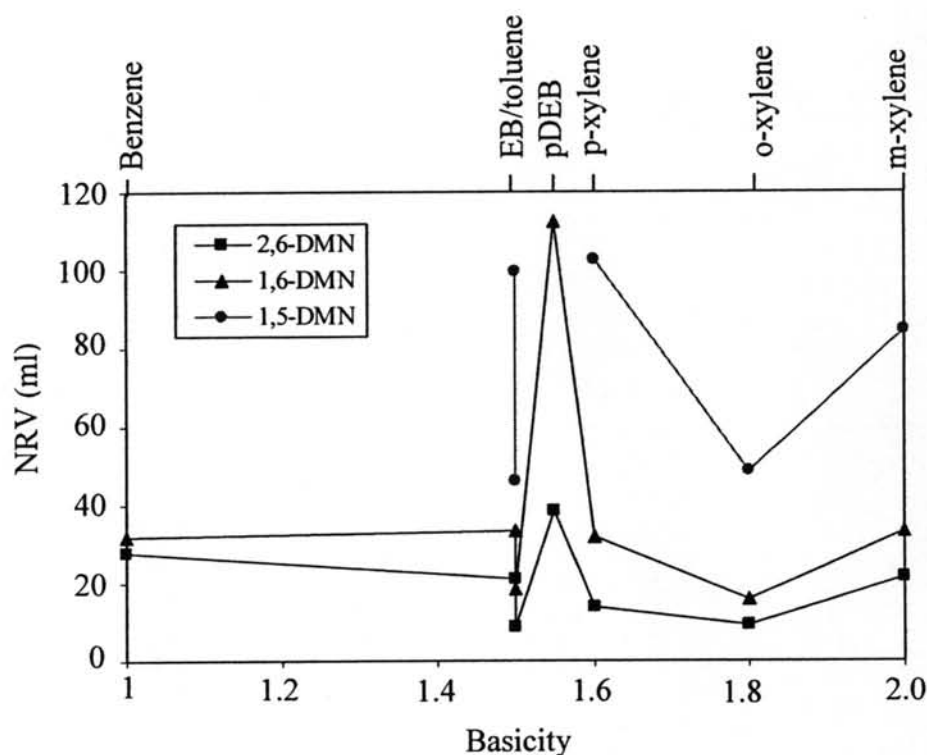
Figure 4.22 Correlation plot between basicity of different desorbents and the NRV of DMNs on NaX.

Despite the close basicity of EB and toluene, the toluene shows much lower NRVs of the three isomers than EB. The strongest desorption of the DMNs are from toluene and o-xylene, while the weakest one is from pDEB. As reported by Suntornpun (2002), o-xylene interacts more strongly than the other C_8 aromatics; this then explains the strong desorption of o-xylene in our experiment. However, the tendency of the NRVs from the effect of the basicity cannot be simply interpreted. Consequently, the figure clearly informs that the acid-base interaction does not dominate the adsorptivity of all desorbents, except o-xylene.

Because NaX is a high polar zeolite, the dipole-dipole interaction between the zeolite and polar compounds could be strong. Then, it is anticipated that this interaction should play an important role in the desorption. The higher the dipole moment of the desorbent is, the stronger the interaction should be. Figure 4.23 was

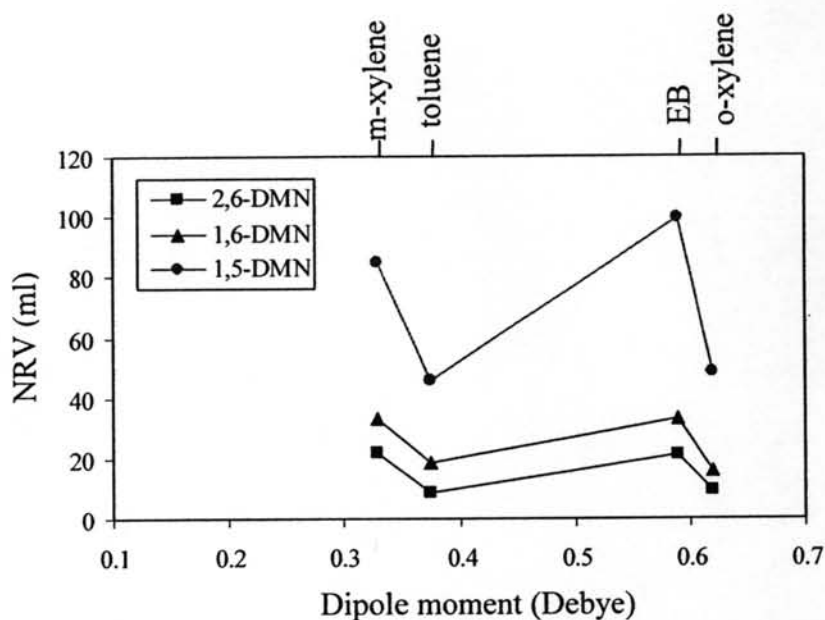then constructed to investigate the relationship between the dipole moment of desorbents and the NRVs.

Figure 4.23 Correlation plot of the dipole moment from different desorbents and the NRV on NaX.

Figure 4.23 shows that there is no common tendency to explain the relationship between the dipole moment from the desorbents and the NRV. Then, the dipole moment effect from the desorbents might not be considerable. Comparing the relationship of the NRVs with the basicity in NaX with that in NaY, the NRVs from both zeolites reach the maximum at the basicity of pDEB. For the other desorbents, the NRV trends between NaY and NaX are different. This dissimilarity is also found with the tendency of the NRVs from the different dipole moments of the desorbents.

On one hand, the high NRVs of DMNs observed in the pDEB system suggests the influence of the steric hindrance in the same way as what has already been discussed in the NaY part. The rate-selective mechanism is dominated in the pDEB desorption without another specific interaction. On the other hand, the distinguished behavior between these two adsorbents in each desorbent system

indicates the role of the acidic behavior of the adsorbents to the adsorption of DMNs as discussed in Kraikul *et al.* (2006b). In order to investigate this hypothesis, a correlation plot was made between the zeolite acid strength represented by the Sanderson's intermediate electronegativity (S_{int}) and the NRVs, as shown in Figure 4.24. The higher S_{int} indicates high electron-accepting ability and strong adsorbent acidity (Barthomeuf, 1996). The zeolite acidity is known to be adjusted by changing a number of atoms in one unit cell. In this work, NaX and NaY with Si/Al_2 ratios of 2.5 and 5.0 designated by 2.5NaX and 5.0NaY were used. By varying the Si/Al_2 ratio, a number of atoms in one unit cell are changed. From 2.5NaX to 5.0NaY, the zeolite acidity increases, and then the S_{int} increases from 3.17 to 3.69.

As shown in Figure 4.24, the adsorbability of the DMNs evidently depends on the acid properties of the adsorbent. The NRV of 2,6-DMN decreases as the Sanderson's electronegativity increases. Despite being the rejective isomer, 2,6-DMN is observed in Figure 4.21 having the interaction with NaX in every desorbent system while there are only the EB and pDEB systems for NaY. As well as 2,6-DMN, the increase in 1,5-DMN interaction is shown toward NaX. In contrast, the adsorption of 1,6-DMN does not improve much by changing NaY to NaX adsorbent. The adsorption of 1,6-DMN seems to depend on the desorbents. With benzene, p-xylene, m-xylene, and pDEB, the NRV decreases as the acid strength increases, while the opposite trend is found with toluene desorbent due to its ability to reverse the selectivity between 1,6-DMN and 1,5-DMN in NaY. The NRV is almost constant when EB and o-xylene are used.

The result reveals that the adsorption of DMNs occurs via the acid-base interaction. However, because the order of the preferential adsorption is 1,5DMN > 1,6-DMN >2,6-DMN, one may expect 1,5-DMN to be more basic than 2,6-DMN. Consequently, when NaY is changed to NaX, which has lower acidity, the NRV of 1,5-DMN should reduce. Therefore, it suggests other parameters should be taken into account.

This result corresponds to that reported by Kraikul *et al.* (2006b). The preferential adsorption of 1,5-DMN on X-zeolites takes place instead of on Y-zeolites, and only on Li-FAU and Na-FAU zeolites among the employed alkali X and Y adsorbents. When the adsorbent is changed from NaY to NaX zeolite, there

are extra cations positioned on sites III (SIII) or III' (S III'), which are unoccupied in Y-type zeolites. A zeolite consists of two adsorption sites; that is, cation and oxygen framework. Nevertheless, it is usually cation sites that are more important, as found with the adsorption of the C_8 aromatics. We believe this is also true for DMNs adsorption. The extra cations may enhance the interaction of the naphthalene aromatic rings by enabling the closer interaction. A reasonable hypothesis of the interaction consists of the interaction of one aromatic ring of DMNs with S II cations with a simultaneous interaction of another aromatic ring with S III cations, as suggested by Laborde-Boutet $et\ al.$ (2006). This hypothesis would not work in huge cationic sites since one adsorbate molecule would lack its accesability. As the Na^+ is considered to be a small size in the alkali metal group, its high polarizability then allows 1,5-DMN adsorbate to access and interact with.

On the other hand, the extra cations are known to disturb the arrangement of many adsorbate molecules; for example, benzene (Daems $et\ al.$, 2006) and toluene (Laborde-Boutet $et\ al.$, 2006). Possibly due to this obstruction, the desorbents, i.e. benzene, p-xylene, m-xylene, and EB, do not interact well with NaX and then result in the high NRV in our study. The obstacle of the interaction of the desorbent and the feasible adsorption of the DMNs both results in the increase in the 1,5-DMN adsorptivity, but to a different degree depending on a desorbent.

For 1,6-DMN, the adsorptivity should be controlled by other parameters besides what was discussed beforehand. The competitive adsorption of the isomer with EB and o-xylene is revealed because of no change in the NRV along the increase in the acidity. In other words, the change of the adsorptivity of the desorbents and 1,6-DMN is in the same order. So, it suggests that 1,6-DMN should not increase its interaction with the extra cations in NaX. While the adsorption of desorbents (benzene, m-xylene and p-xylene) may decrease and the adsorption of 1,6-DMN stays relatively the same, high NRV from NaX is observed. However, further investigation is still needed to prove the hypothesis.
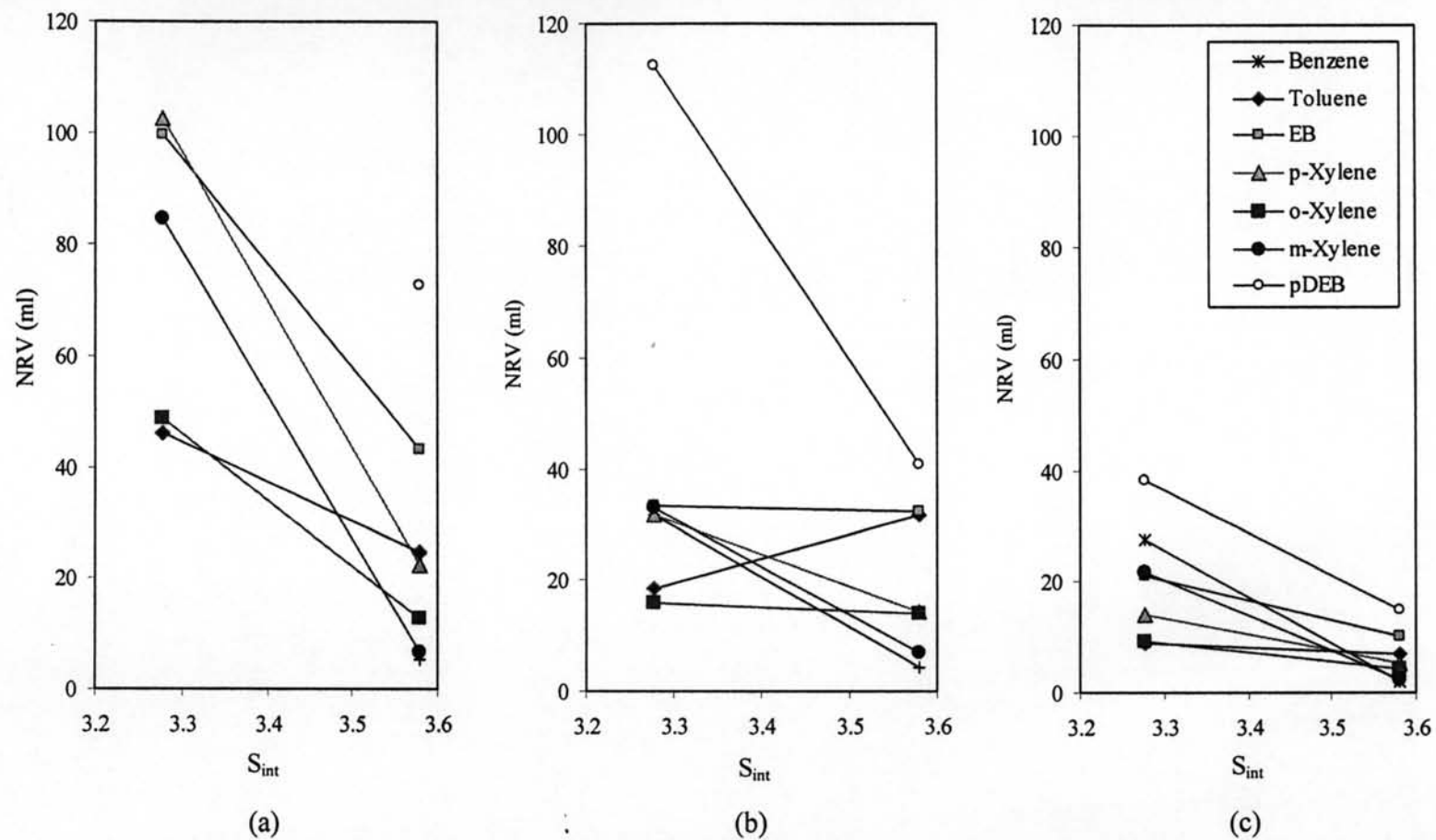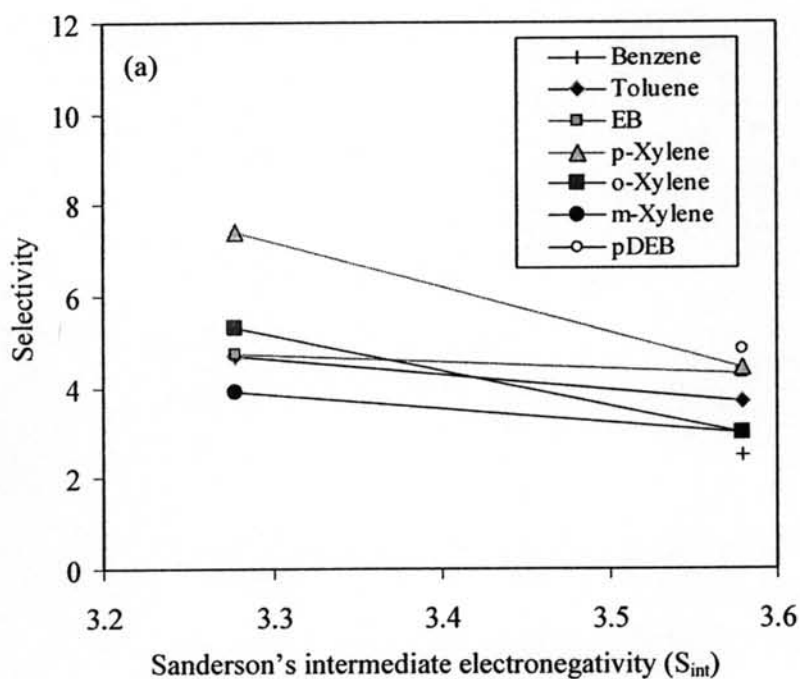
Figure 4.24 Correlation plot between the Sanderson's intermediate electronegativity (S_{int}) and the NRV of (a) 1,5-DMN, (b) 1,6-DMN, and (c) 2,6-DMN.

As far as the separation is concerned, the separation of 1,6-DMN from 2,6-DMN is a problem found with NaX more than with NaY since 2,6-DMN also interacts with NaX. In Figure 4.25, the selectivity of 1,6-DMN and 1,5-DMN over 2,6-DMN is plotted with the Sanderson's intermediate electronegativity (S_{int}). The selectivity shows the opposite trend with the zeolite acidity. As the zeolite acidity increases, 2,6-DMN can be better separated from 1,6-DMN, but worse from 1,5-DMN. However, the separation overall has good performance due to the high selectivity. Therefore, even though the separation can be accomplished only in the 2,6-DMN rejective system, the result suggests the possibility to obtain successful 2,6-DMN purification.
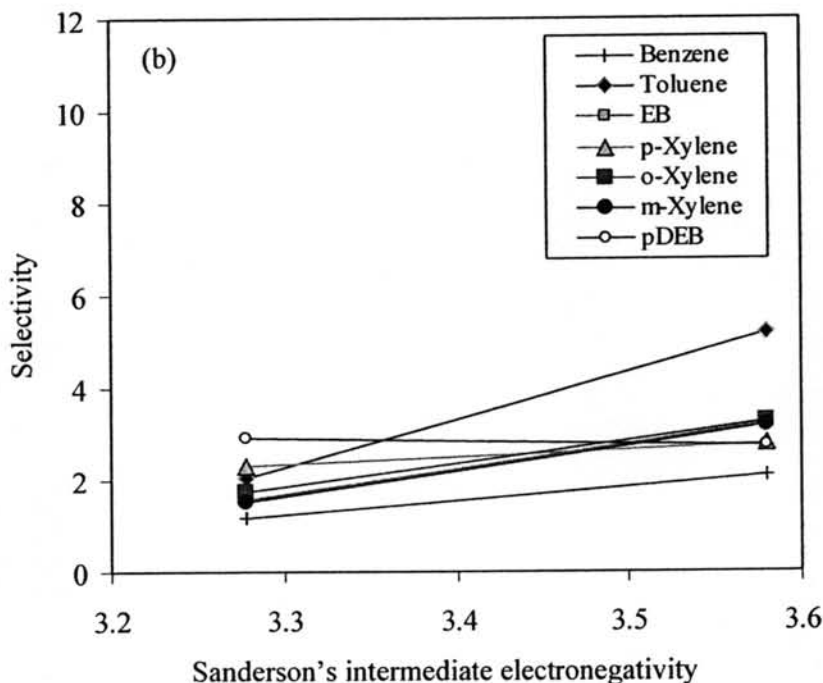
Figure 4.25 Correlation plot between the Sanderson's intermediate electronegativity and the selectivity of: (a) 1,5-DMN over 2,6-DMN, and (b) 1,6-DMN over 2,6-DMN.

4.2.3 Effect from Si/Al$_2$ Ratio

Since the DMNs separation is dominated by the acid-base interaction between DMN and adsorbent, the effect of the acidic characteristic of the adsorbent was studied in this part. Different Si/Al$_2$ ratio zeolites including 2.0 and 12.0 designated by 2.0NaX and 12.0NaY, respectively, were used. Three desorbents-EB, toluene, and p-xylene-were employed because of their good DMNs separation performance, as shown in the two former parts (4.2.1 and 4.2.2). The elution profiles from 12.0NaY are shown in Figure 4.26. The three desorbents provide similar elution profiles with no separation among the DMNs. The high acid zeolite strongly interacts till no difference of the adsorptivity among the three DMN isomers can be observed. It also interacts well with the desorbents, and then results in narrow peaks and low NRVs, as seen in Figure 4.27. The similarity

found in the three desorbent systems may also result from a too strong interaction from 12.0NaY.

Because the pore size of the zeolite becomes smaller with the increase in the Si/Al$_2$ ratios (Guo *et al.*, 2000), one possible reason for unfavorable adsorption of DMNs is from their bulky naphthalene molecules. The DMN molecule cannot compete with the smaller desorbents, and then results in strong desorption. In addition, the number of Na$^+$ ions is reduced when the silica framework enhances. Hence, DMNs have a weaker interaction with the adsorbent due to the lack of cation sites. Therefore, the result substantiates that the cation sites are more important than the negative oxygen sites as DMNs adsorption sites.
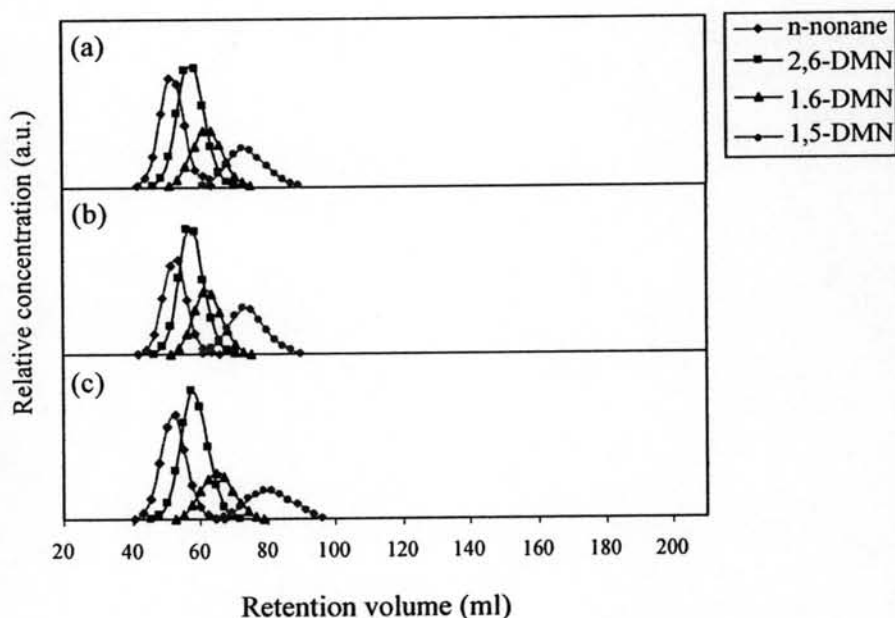

Figure 4.26 Elution profile of 1,5-, 1,6-, and 2,6-DMN on 12.0NaY at 1 h^{-1} LHSV, 180°C from different desorbents: (a) EB, (b) toluene, and (c) p-xylene.
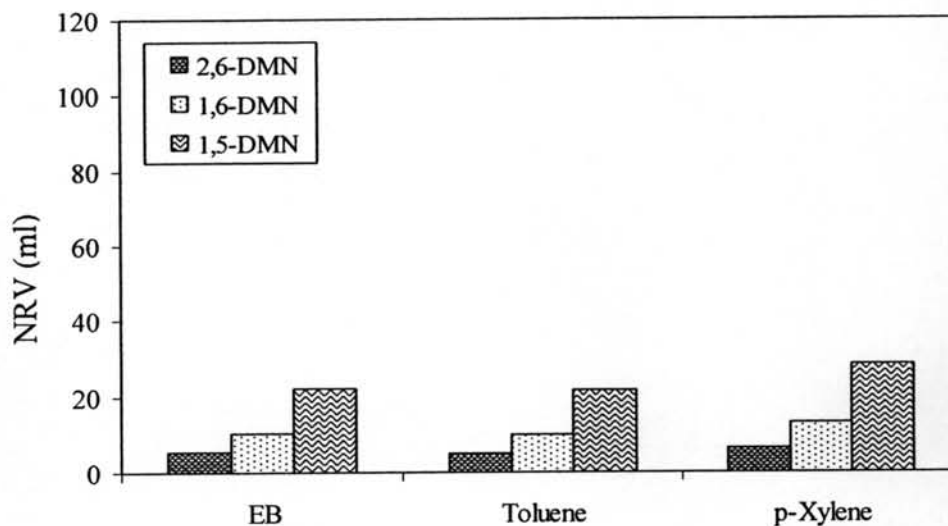
Figure 4.27 NRVs of 1,5-, 1,6-, and 2,6-DMN on 12.0NaY with EB, toluene, and p-xylene desorbents.

The adsorption over 2.0NaX elution profiles are shown in Figure 4.28. The bar chart of the NRVs is also illustrated in Figure 4.29. The adsorption of 1,5-DMN shows the highest affinity toward the zeolite followed by 1,6-DMN and 2,6-DMN. The adsorption of 2,6-DMN can be seen in all systems. Although the separation depends on the desorbents, with the EB and toluene desorbents, the separation performance is not considerably different. From lower NRVs, toluene provides slightly stronger desorption. However, both cannot accomplish 2,6-DMN purification since there is hardly any difference between the interaction of 2,6-DMN and 1,6-DMN. p-Xylene shows the best separation among the three isomers.
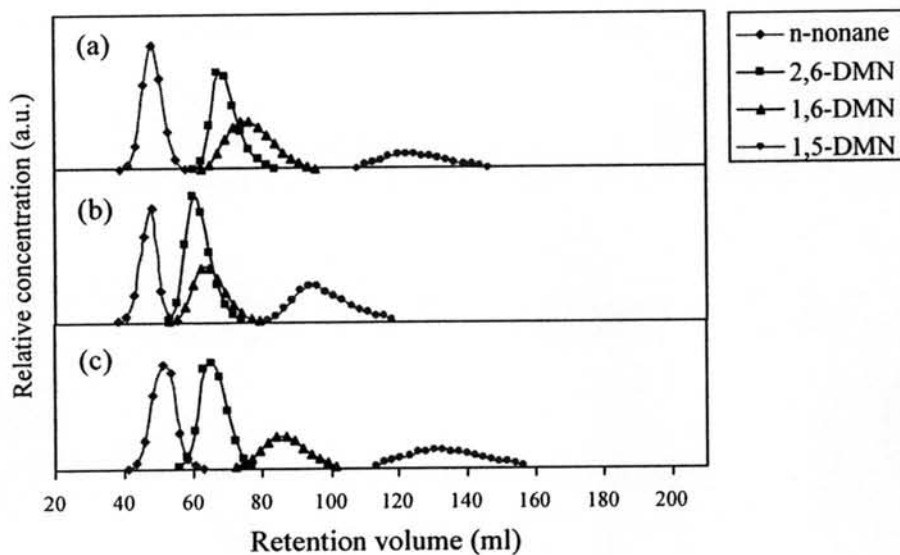
Figure 4.28 Elution profile of 1,5-, 1,6-, and 2,6-DMN on 2.0NaX at 1 h^{-1} LHSV, 180°C from different desorbents: (a) EB, (b) toluene, and (c) p-xylene.
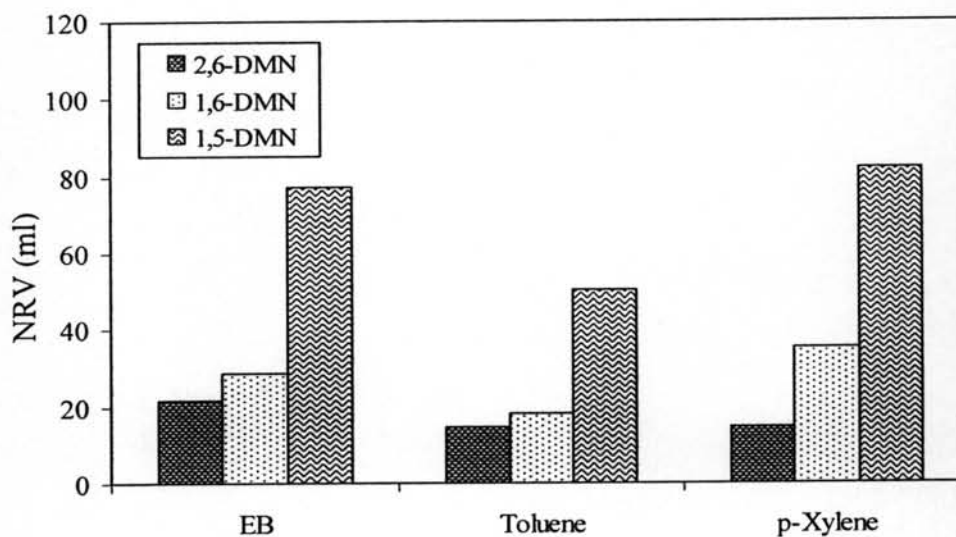

Figure 4.29 NRVs of 1,5-, 1,6-, and 2,6-DMN on 2.0NaX with EB, toluene, and p-xylene desorbents.

In order to elucidate the effect from the Si/Al$_2$ ratio, the results from 2.0NaX and 12.0NaY are compared with those from 2.5NaX and 5.0NaY. The

NRVs are plotted with the Sanderson's intermediate electronegativity for EB, toluene, and p-xylene desorbents in Figure 4.30 (a), (b), and (c) respectively. As the Si/Al_2 ratio increases, the Sanderson's electronegativity increases.
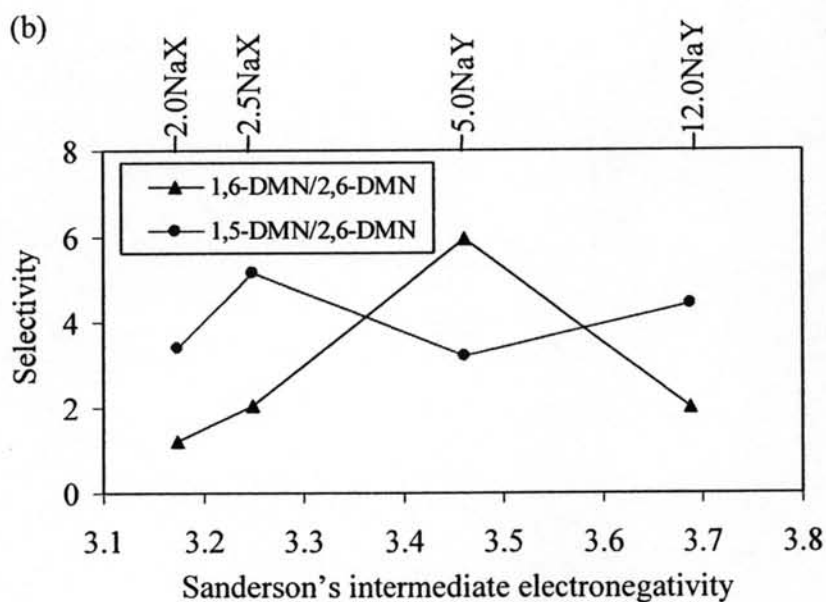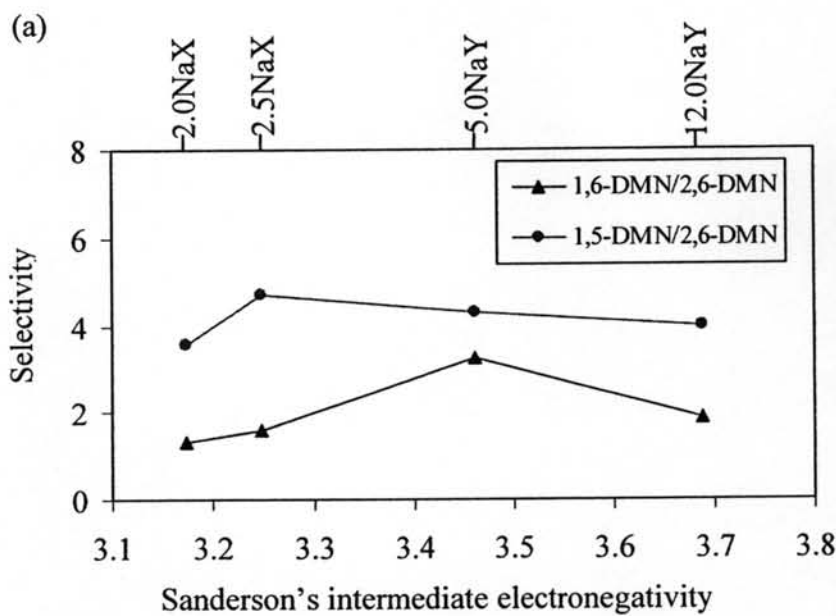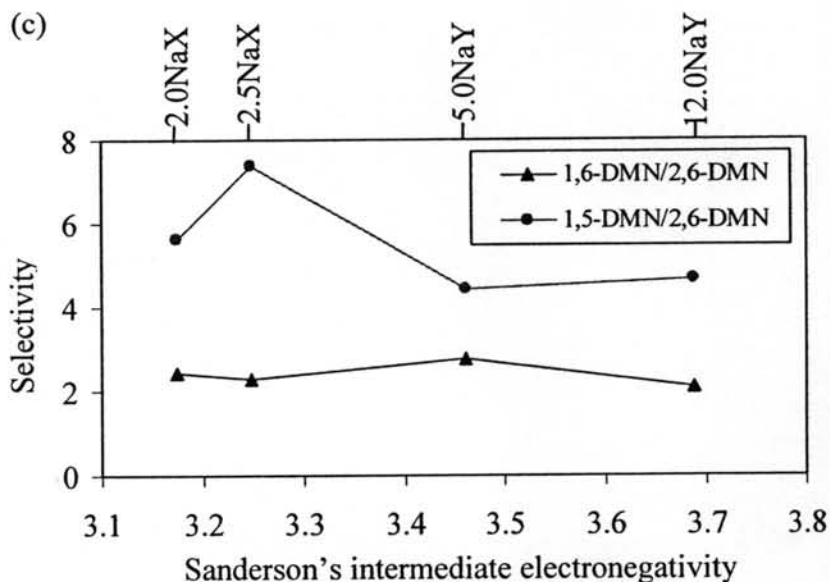
Figure 4.30 Correlation plot between the Sanderson's intermediate electronegativity and the selectivity of 1,6-DMN and 1,5-DMN over 2,6-DMN from different desorbents: (a) EB, (b) toluene, and (c) p-xylene.

The result reveals that the specific interaction of the three desorbents is involved in the separation along with the effect from the acid properties of the zeolite. At the lowest S_{int}, the number of cation atoms is highest, so one may expect strong 1,5-DMN-cation interaction. However, the preferential adsorption of 1,5-DMN at this S_{int} is decreased to be lower than that at the S_{int} of 2.5NaX. This suggests the disturbance of a cation toward 1,5-DMN. 2.5NaX possesses the maximum in the selectively adsorption of 1,5-DMN over 2,6-DMN. After that, the selectivity is constant in EB, and decreases in toluene and p-xylene. Hence, the acidity of the adsorbent hardly affects the 1,5-DMN adsorption in the EB system. After the dramatic decrease to the S_{int} of 5.0NaX, the selectivity of 1,5-DMN over 2,6-DMN increases again at 12.0NaY in toluene, while it is rather constant in p-xylene.

A different tendency is found with the selectivity of 1,6-DMN over 2,6-DMN. EB and toluene show a similar trend in that the selectivity increases with the acidity to the maximum at the S_{int} of 5.0NaX before decreasing. The

selectivity of 1,6-DMN over 2,6-DMN does not depend on the acidity in the p-xylene system. Interestingly, the Na exchanged FAU zeolite can be adjusted to preferentially adsorb 1,6-DMN only with the toluene desorbent at the Si/Al_2 ratio of 5.0.