

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Single Component Adsorption

Single component adsorption isotherms for n-paraffin and n-olefin with carbon numbers 6, 8, 10, 12, 14, 16, 18 and 20 on silicalite were obtained at room temperature (~25 °C) are shown with the circle symbol in Figures 4.1 to 4.16. The equilibrium adsorbed capacity (Q) is expressed in the number of molecules adsorbed per unit cell. The adsorption isotherms can be fitted with a double site Langmuir (DSL) model, equation 4.1. The model takes into account the geometrical constraint of the silicalite pore structure (Zhu *et al.*, 1998). The difference between the channels and the intersections is much larger than the difference between the two types of channels. This means that essentially two different adsorption sites exist in silicalite.

$$Q = \frac{(Q_{\max,I})(C_e)}{Kd_I + C_e} + \frac{(Q_{\max,C})(C_e)}{Kd_C + C_e} \quad (4.1)$$

C_e refers to the equilibrium concentration, Q_{\max} is the maximum capacity, and Kd is equilibrium dissociation constant. The subscriptions I and C refer to the intersections and channels, respectively. Saturation capacity is defined as the maximum capacity that molecules can pack in the pore of silicalite and it can be obtained from either the plateau regions in the isotherms or summation between $Q_{\max,C}$ and $Q_{\max,I}$.

Overall, the model fits the experimental data well except n-dodecane, 1-dodecene, n-tetradecane, 1-tetradecene. The adsorption isotherms for these hydrocarbons appear to reach the saturation plateau very fast. This is may be due to the matching between the molecules and the silicalite one unit cell length (length of n-dodecane, n-tetradecane and one unit cell are 1.8, 2 and 2 nm, respectively). Estimated parameters in equation 4.1 are summarized in Appendix A3.1.

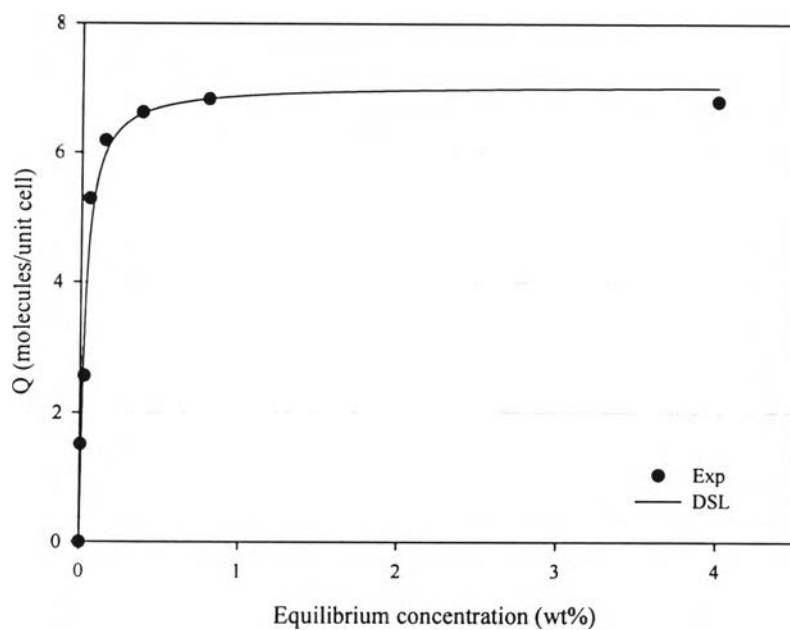


Figure 4.1 Adsorption isotherm for n-hexane at 25 °C.

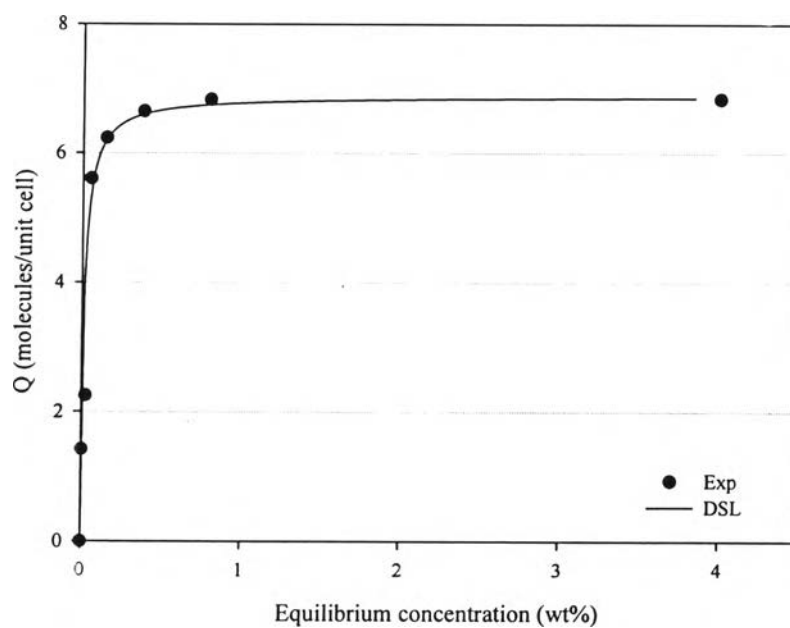


Figure 4.2 Adsorption isotherm for 1-hexene at 25 °C.

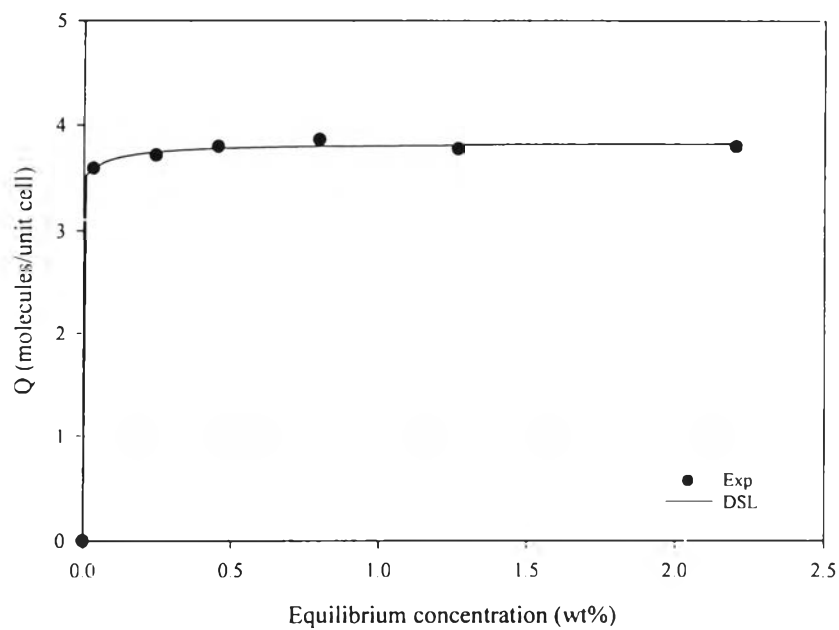


Figure 4.3 Adsorption isotherm for n-octane at 25 °C.

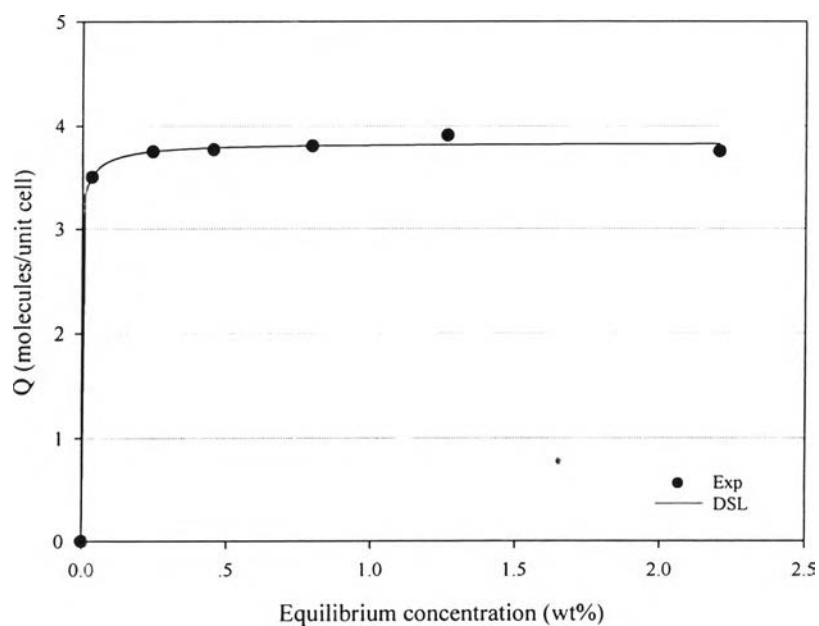


Figure 4.4 Adsorption isotherm for 1-octene at 25 °C.

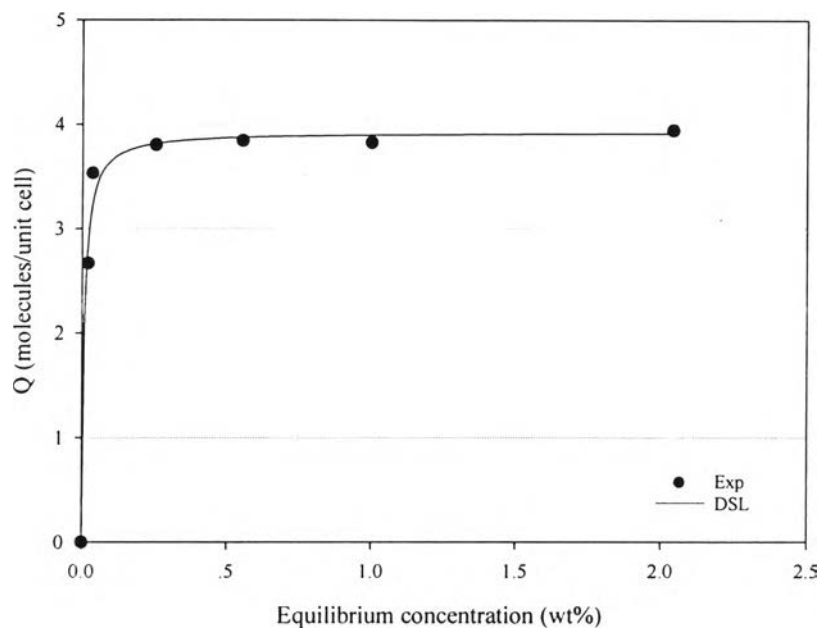


Figure 4.5 Adsorption isotherm for n-decane at 25 °C.

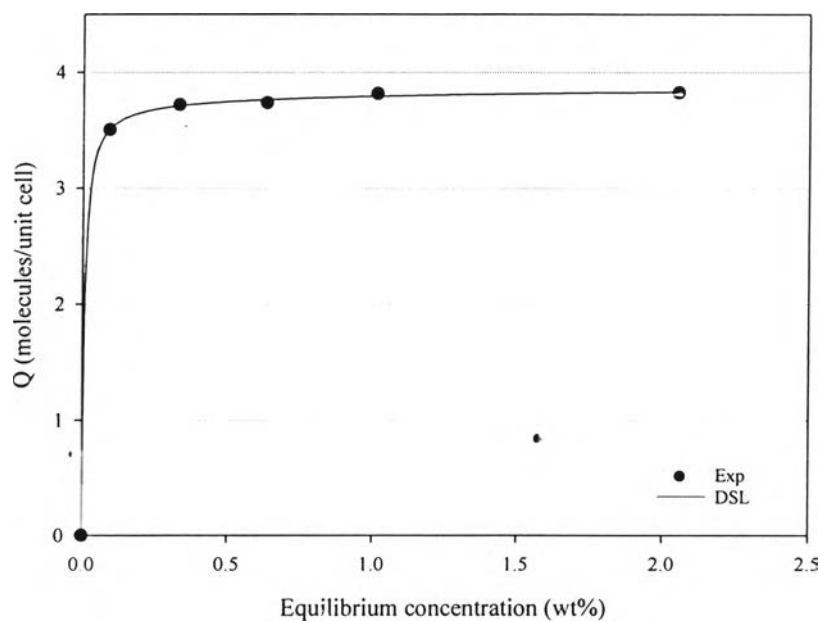


Figure 4.6 Adsorption isotherm for 1-decene at 25 °C.

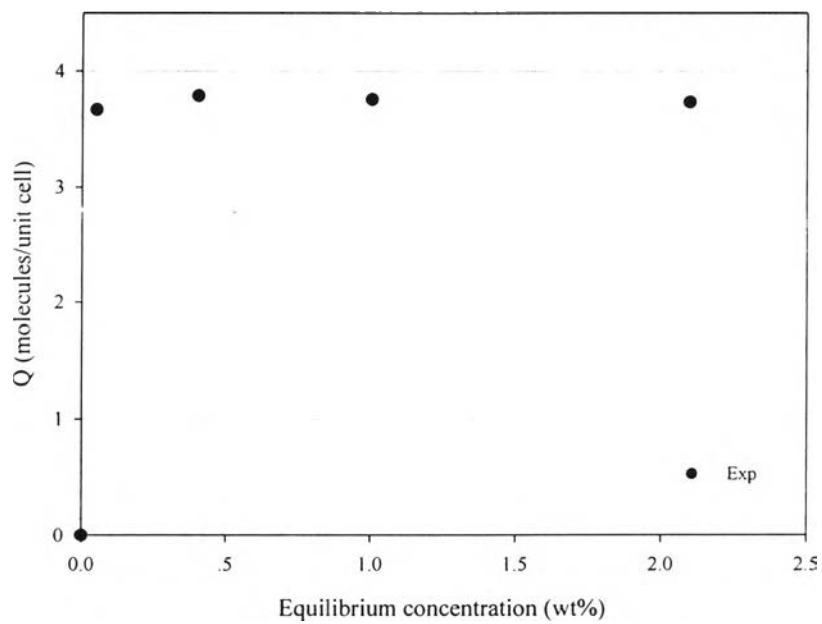


Figure 4.7 Adsorption isotherm for n-dodecane at 25 °C.

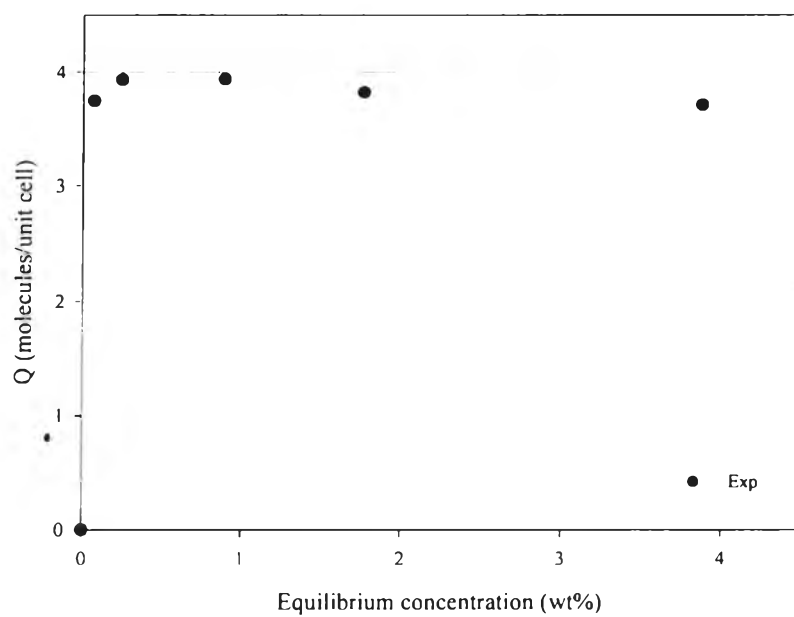


Figure 4.8 Adsorption isotherm for 1-dodecene at 25 °C.

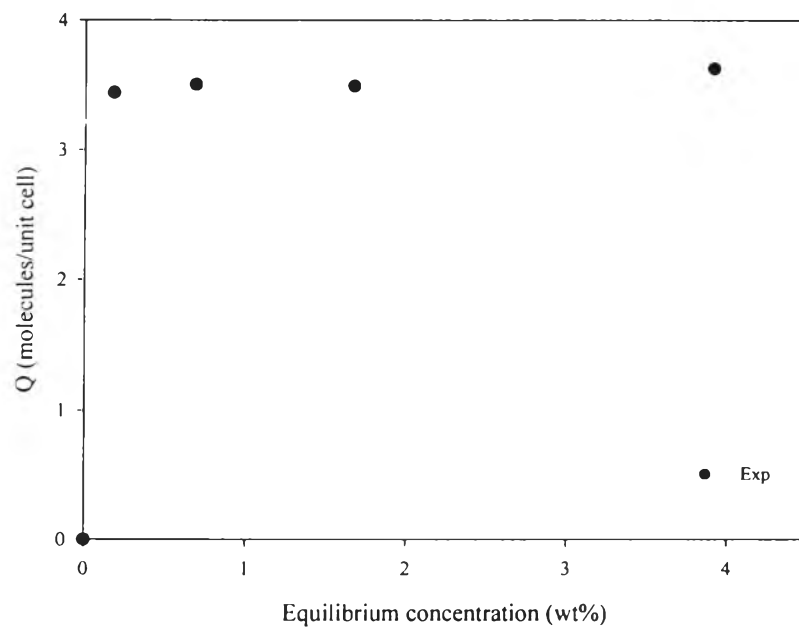


Figure 4.9 Adsorption isotherm for n-tetradecane at 25 °C.

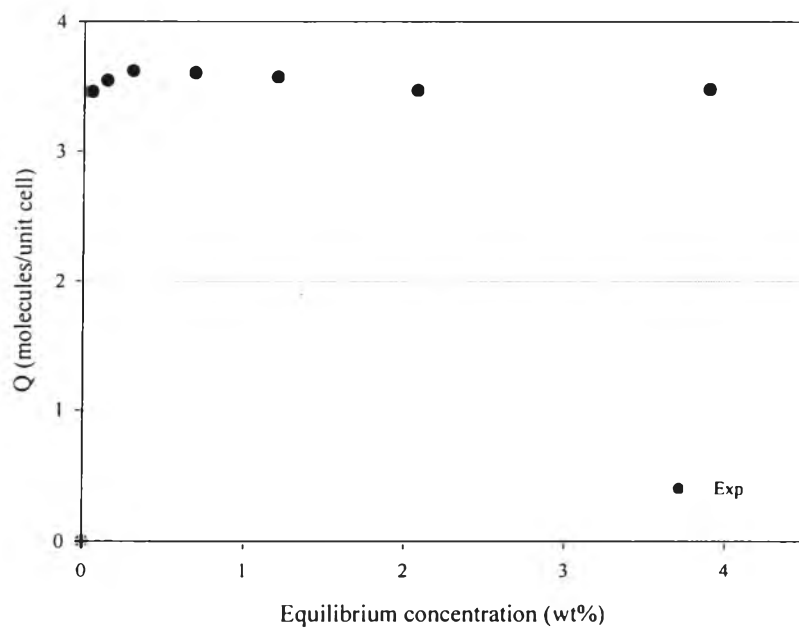


Figure 4.10 Adsorption isotherm for 1-tetradecene at 25 °C.

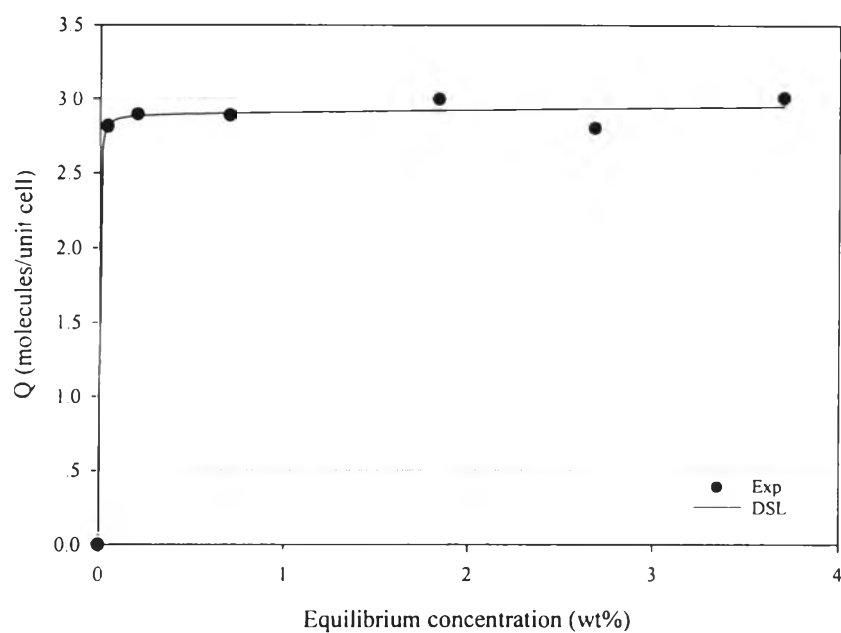


Figure 4.11 Adsorption isotherm for n-hexadecane at 25 °C.

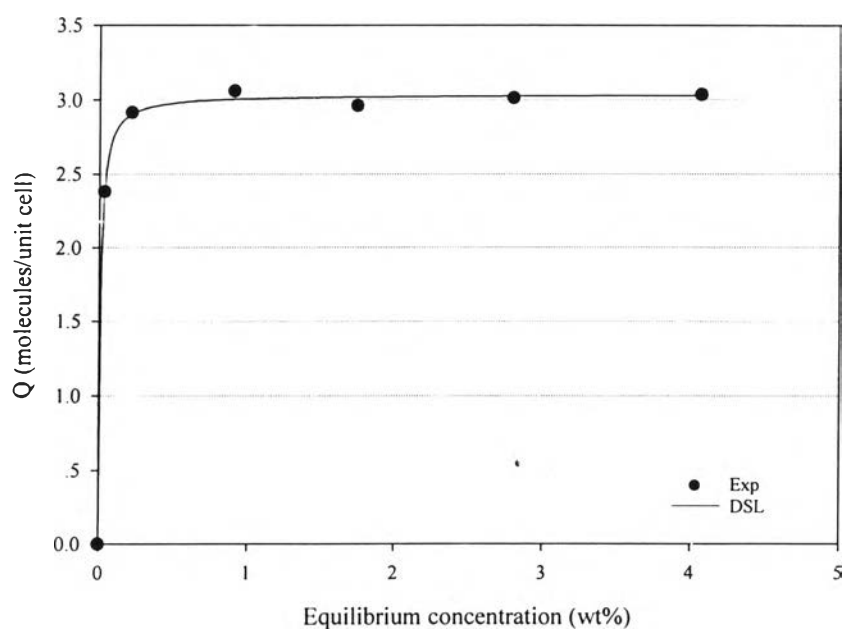


Figure 4.12 Adsorption isotherm for 1-hexadecene at 25 °C.

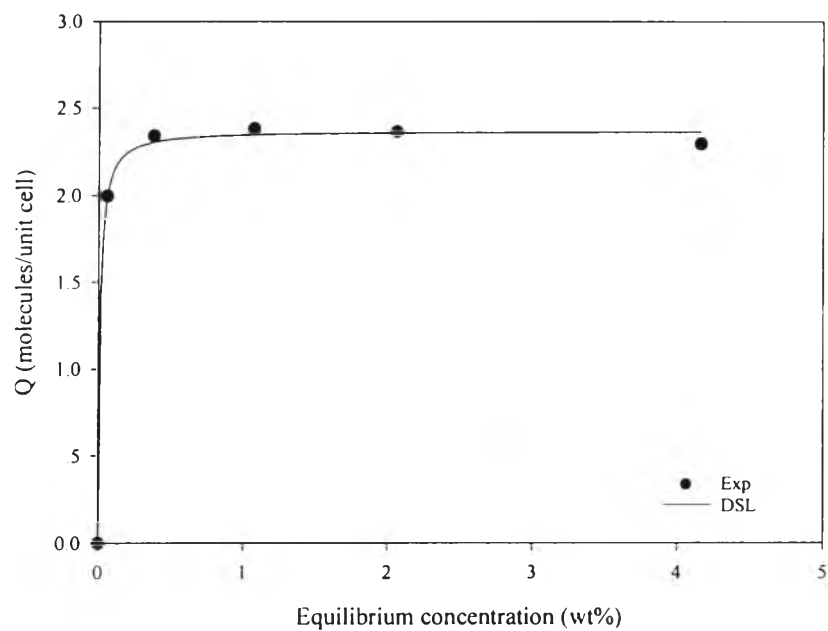


Figure 4.13 Adsorption isotherm for n-octadecane at 25 °C.

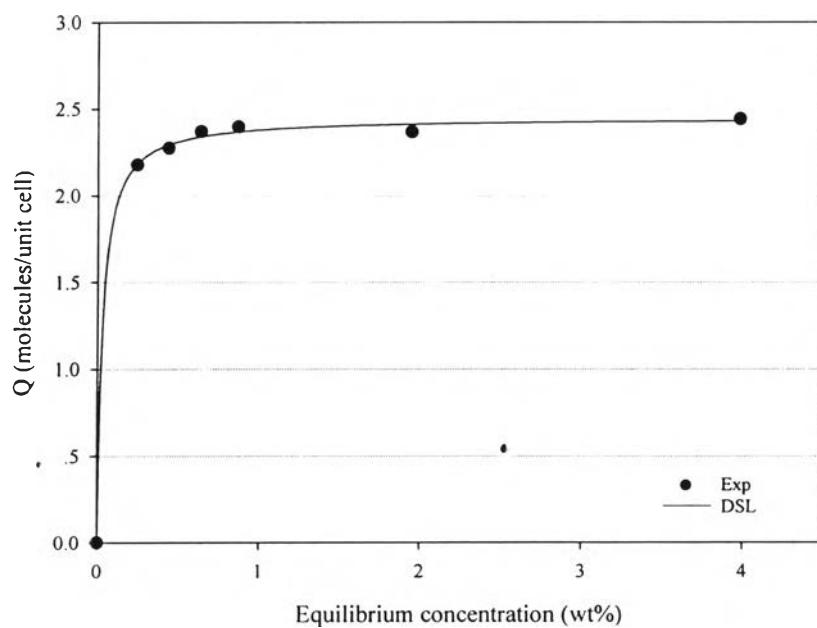


Figure 4.14 Adsorption isotherm for 1-octadecene at 25 °C.

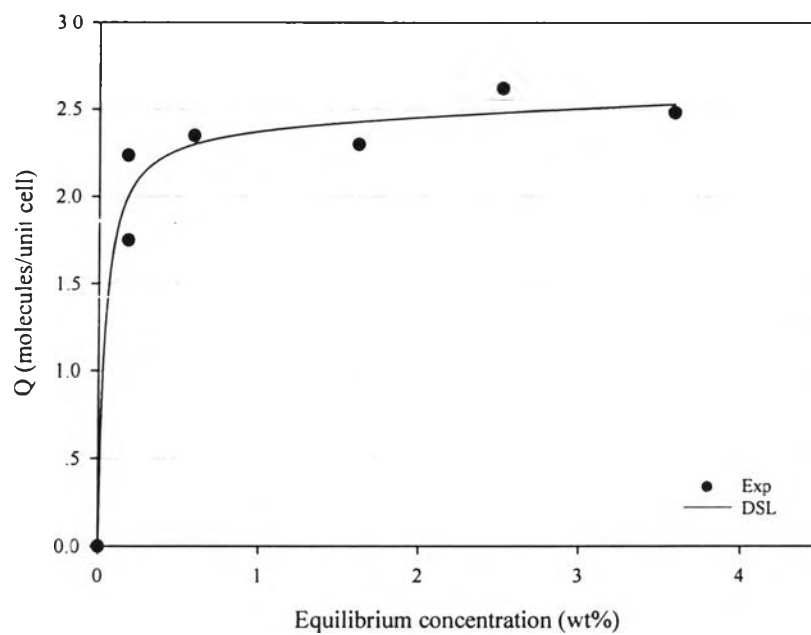


Figure 4.15 Adsorption isotherm for n-eicosane at 25 °C.

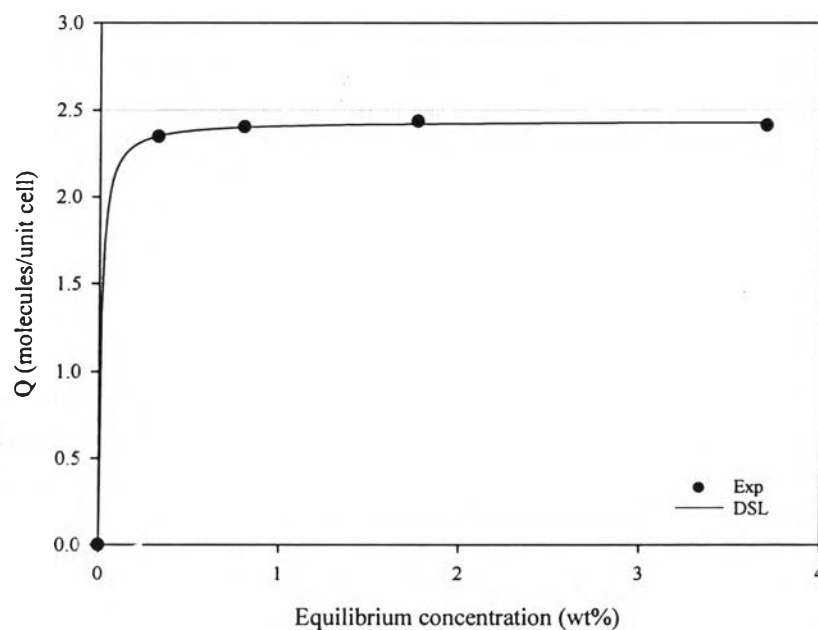


Figure 4.16 Adsorption isotherm for 1-eicosene at 25 °C.

Figure 4.17 compiles saturation capacities in terms of molecules adsorbed and carbon atoms adsorbed per unit cell. The figure shows that the saturation capacities of both n-paraffin and n-olefin in term of molecules adsorbed per unit cell decreases with increasing the carbon number and drop substantially from carbon number 6 to 8. As the length of the n-paraffin and n-olefin uniformly increases with each addition of the CH₂ group, one would expect the saturation capacity to drop linearly with molecular length if all molecules occupy the pores in the same manner. Therefore, the unexpected drop steeply in the saturation capacity of both n-paraffin and n-olefin from carbon number 6 to 8 implies that there may be some differences in the molecule configuration in the pore of silicalite. As reported by De Meyer *et al.* (2003), C₈ and longer alkanes place themselves in different positions in the pore of silicalite from C₆ resulting in a less number of molecules packed per unit cell.

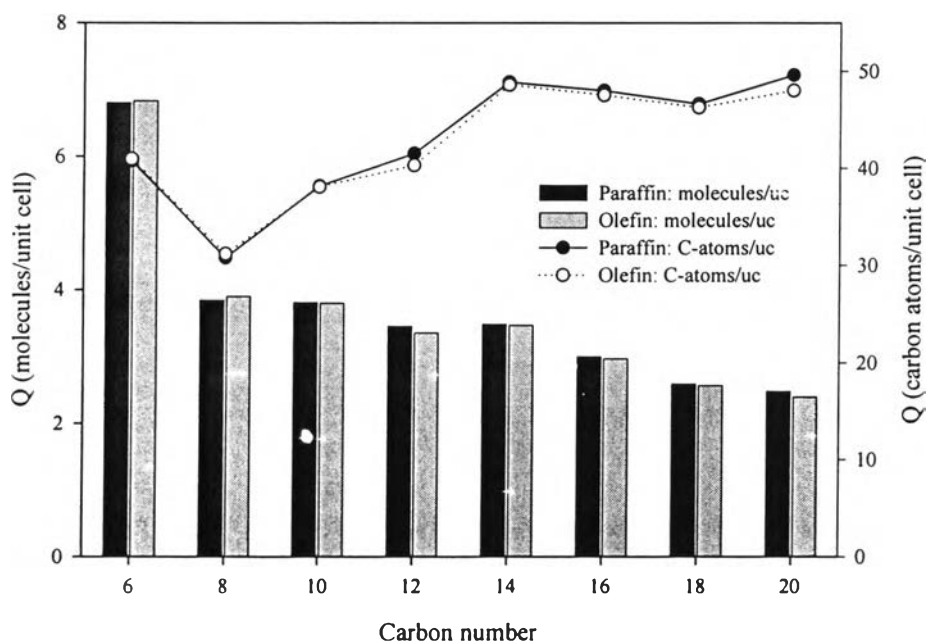


Figure 4.17 Saturation capacities of n-paraffin and n-olefin on silicalite with the carbon numbers ranging from 6 to 20 on silicalite at 25 °C.

Although the number of molecular packing per unit cell in the pore of silicalite decreases rapidly between carbon numbers 6 to 8 and decreases steadily after carbon number 8, the number of adsorbed $-CH_x$ groups per unit cell increases from carbon number 8 on until it reaches a plateau for carbon number 14 to 20. With increasing the chain length, the probability of bending from one channel type to another and of crossing molecules in the intersections becomes larger (De Meyer *et al.*, 2003). The observation that the number of adsorbed $-CH_x$ groups per unit cell remains constant from carbon number 14 on indicates that the pore system of silicalite is very densely packed. For molecules shorter than carbon number 14, it appears that the available space in pores of silicalite is thus not completely used.

In addition, there is no significant difference between n-paraffin and n-olefin saturation capacities at the same carbon number. This may be because the packing efficiency for both n-paraffin and n-olefin is a function of just only the molecular chain length. Therefore, the explanation that used to describe the n-paraffin adsorption on silicalite is also valid for n-olefin.

4.2 Binary Component Competitive Adsorption

Binary component competitive adsorption isotherms for equimolar mixtures of $C_6/1-C_6$, $C_8/1-C_8$, $C_{10}/1-C_{10}$, $C_{12}/1-C_{12}$, $C_{14}/1-C_{14}$, $C_{16}/1-C_{16}$, $C_{18}/1-C_{18}$ and $C_{20}/1-C_{20}$ are shown in Figures 4.18 to 4.25. The total adsorption capacities of silicalite for both components were obtained from the summation of individual adsorption capacities at the same initial concentration. The individual adsorption capacities for n-paraffin and n-olefin are almost the same and approximately half of the total adsorption capacity. The double site Langmuir equation was also applied for binary adsorption isotherms. Most of the binary isotherms fit well with the equation except binary of $C_{10}/1-C_{10}$, $C_{12}/1-C_{12}$ and $C_{14}/1-C_{14}$. The same explanation with single adsorption was also used to describe for this case as well. That is because of the similar between molecules and one unit cell length. The estimated parameters are given in Appendix A3.2. The saturation capacities are also obtained for binary system and it shows the same trend with single adsorption, i.e. the saturation capacities decrease with increasing carbon number and dramatically decrease for

binary of $C_6/1-C_6$ to $C_8/1-C_8$. Total saturation capacities in binary component systems are plotted with saturation capacities in single component as shown in Figure 4.26. The figure shows that the saturation capacities in single component adsorption are comparable with the total saturation capacities in the binary component systems. These results support the idea that the saturation capacities for both n-paraffin and n-olefin strongly depend on molecular chain length with silicalite as the adsorbent.

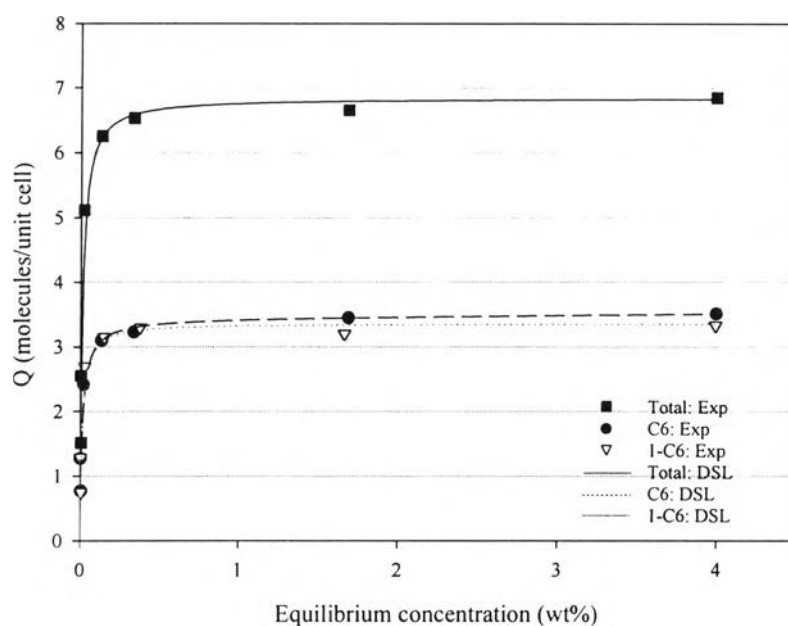


Figure 4.18 Binary adsorption isotherms for n-hexane/1-hexene at 25 °C.

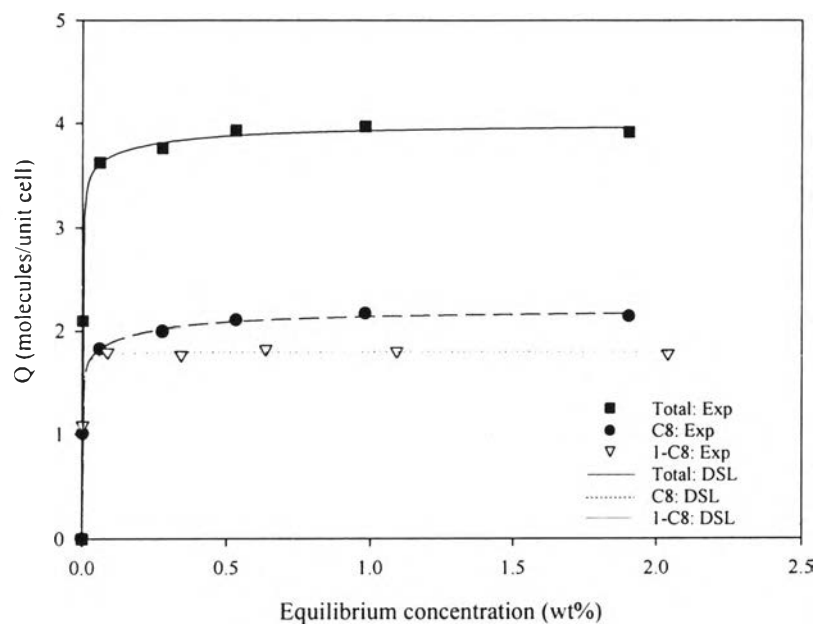


Figure 4.19 Binary adsorption isotherms for n-octane/1-octene at 25 °C.

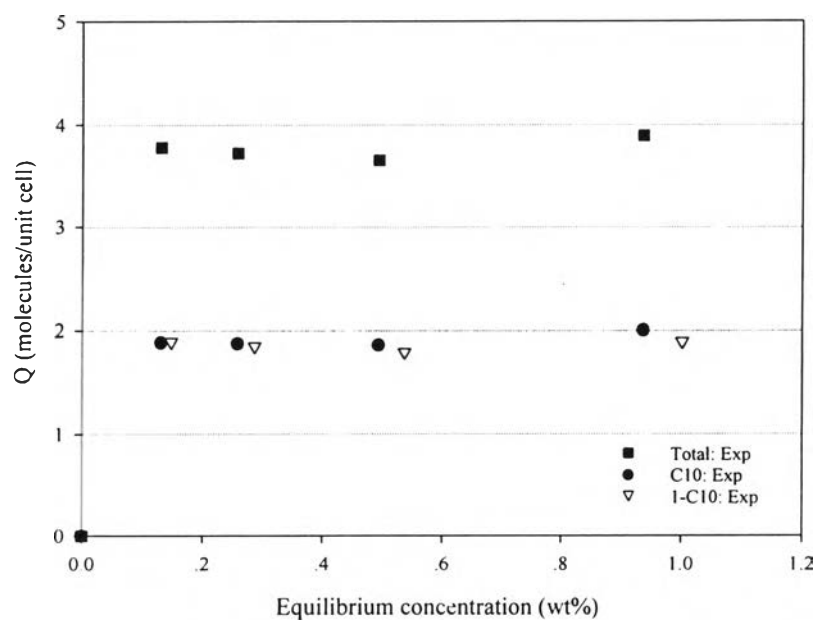


Figure 4.20 Binary adsorption isotherms for n-decane/1-decene at 25 °C.

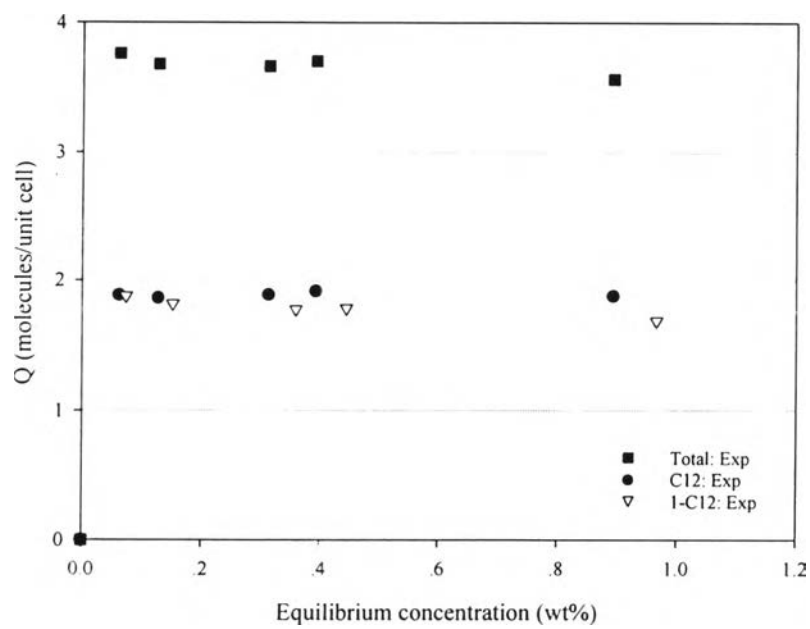


Figure 4.21 Binary adsorption isotherms for n-dodecane/1-dodecene at 25 °C.

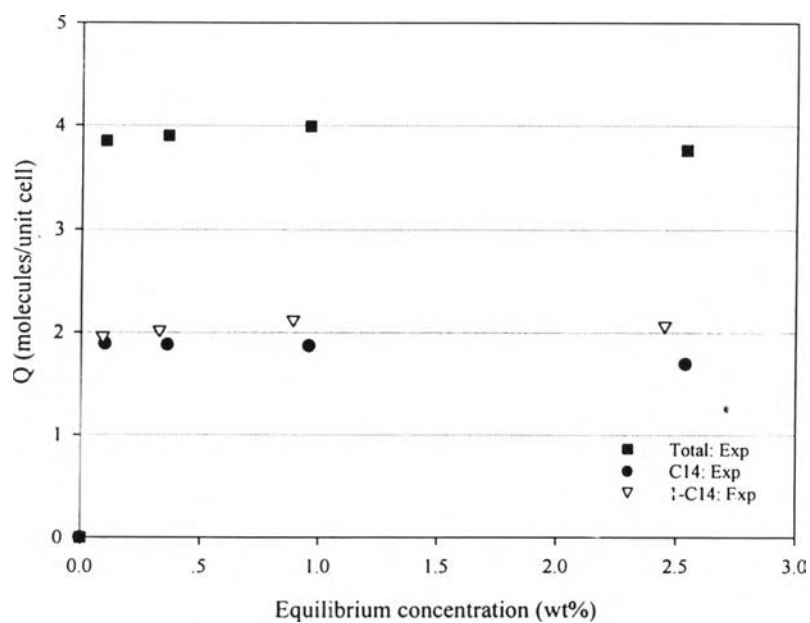


Figure 4.22 Binary adsorption isotherms for n-tetradecane/1-tetradecene at 25 °C.

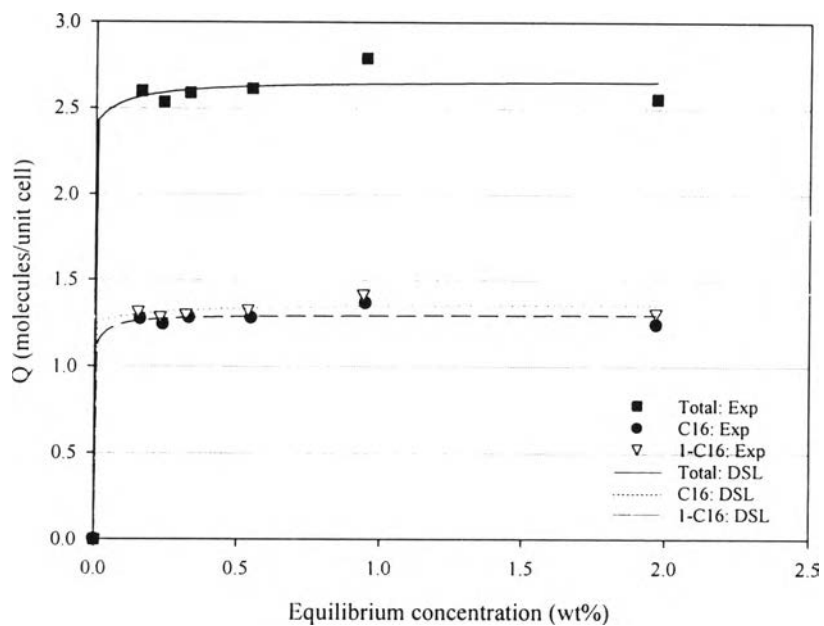


Figure 4.23 Binary adsorption isotherms for n-hexadecane/1-hexadecene at 25 °C.

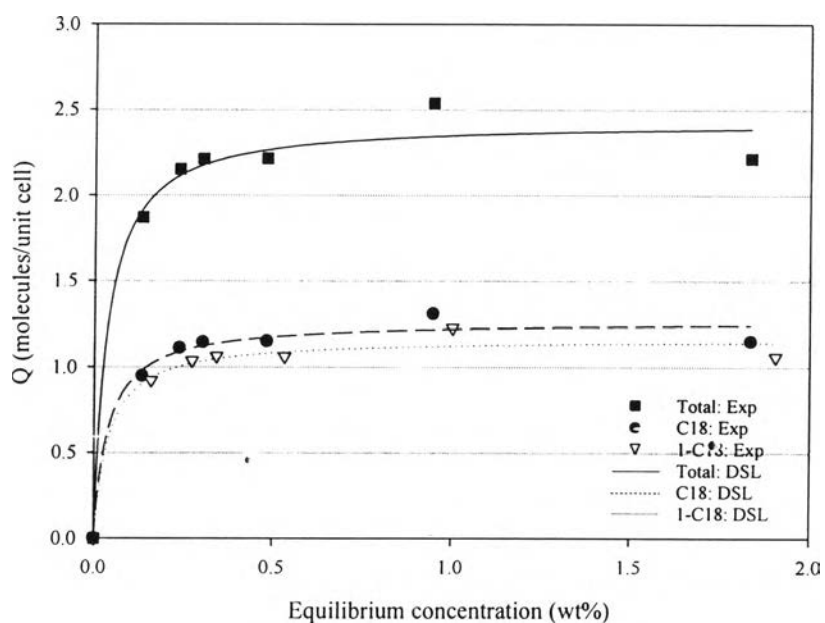


Figure 4.24 Binary adsorption isotherms for n-octadecane/1-octadecene at 25 °C.

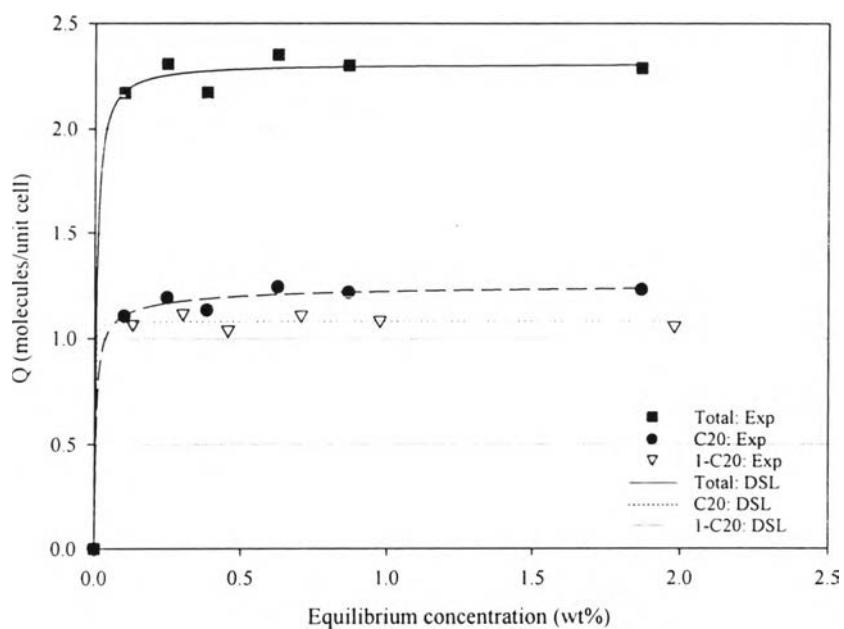


Figure 4.25 Binary adsorption isotherms for n-icosane/1-icosene at 25 °C.

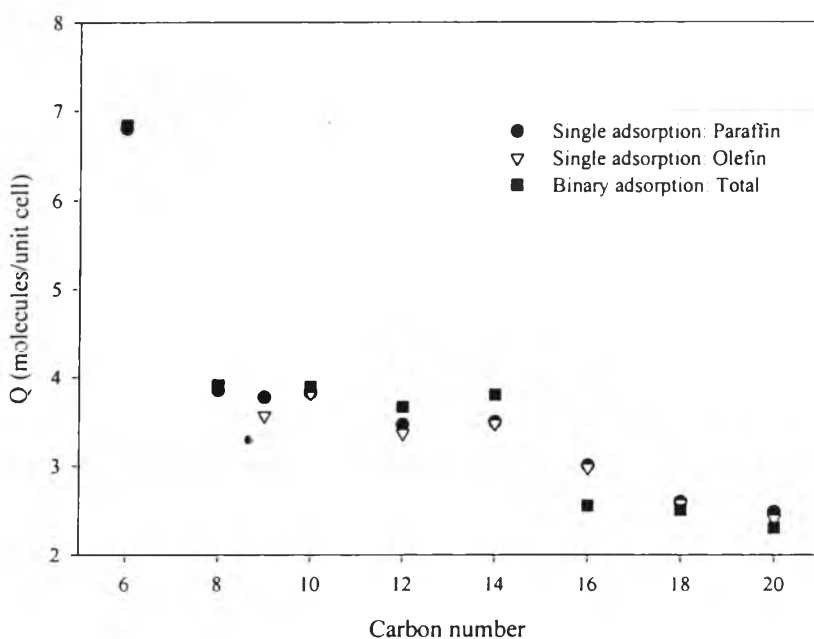


Figure 4.26 Comparison between saturation capacities for single and binary component adsorption for n-paraffin and n-olefin on silicalite at 25 °C.

Selectivities from binary component competitive adsorption isotherms are determined as the equilibrium selectivity and calculated from equation A.1 in Appendix A1.1. Figures 4.27 to 4.34 show the equilibrium selectivities for n-paraffin over n-olefin of the mixtures C₆/1-C₆, C₈/1-C₈, C₁₀/1-C₁₀, C₁₂/1-C₁₂, C₁₄/1-C₁₄, C₁₆/1-C₁₆, C₁₈/1-C₁₈ and C₂₀/1-C₂₀. Results show that the selectivities slightly vary with the concentration. The average values for the equilibrium selectivities for the whole range of studied concentration are shown in Table 4.1.

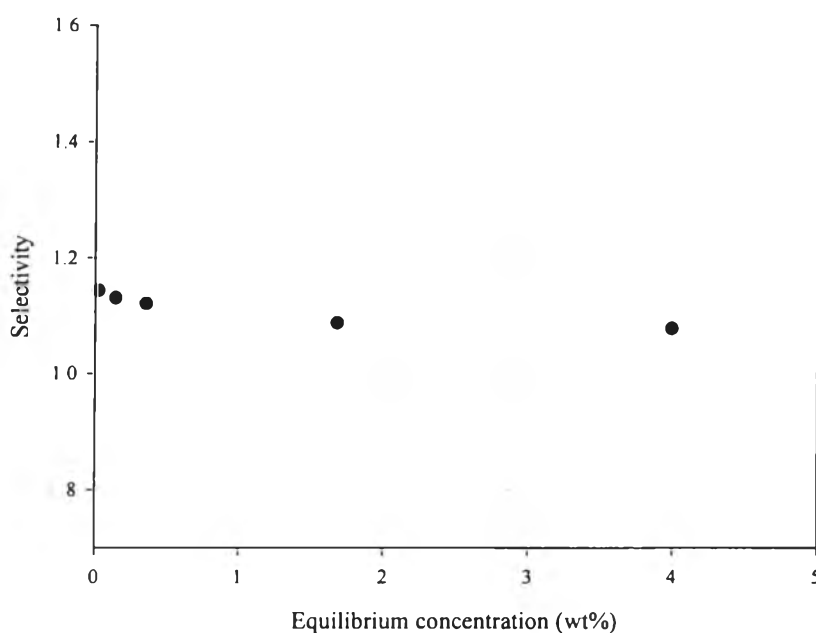


Figure 4.27 Selectivity for n-hexane/1-hexene at 25 °C.

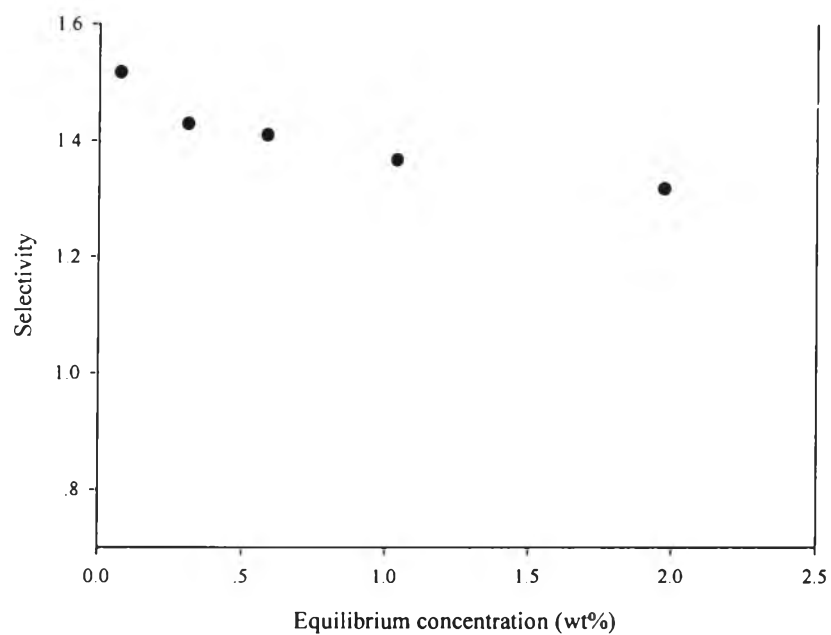


Figure 4.28 Selectivity for n-octane/1-octene at 25 °C.

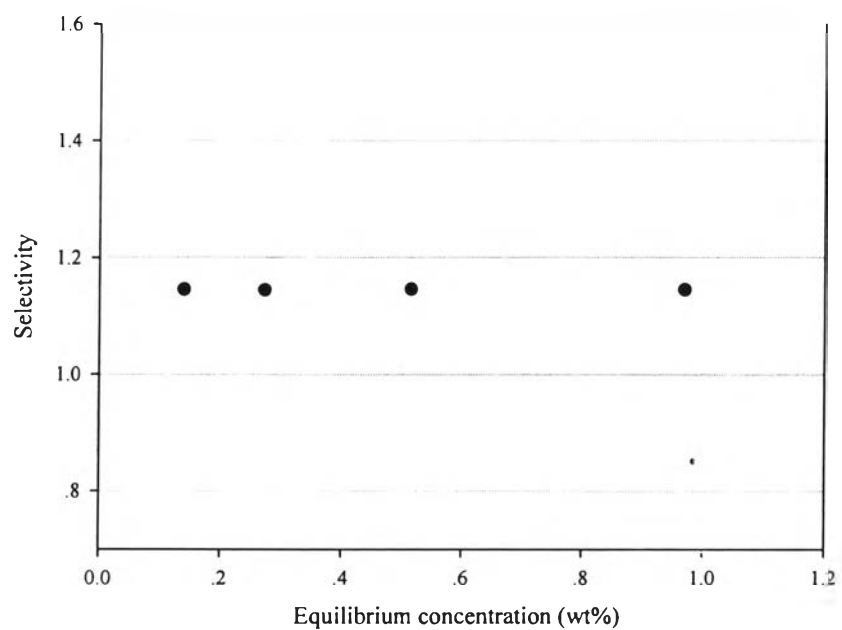


Figure 4.29 Selectivity for n-decane/1-decene at 25 °C.

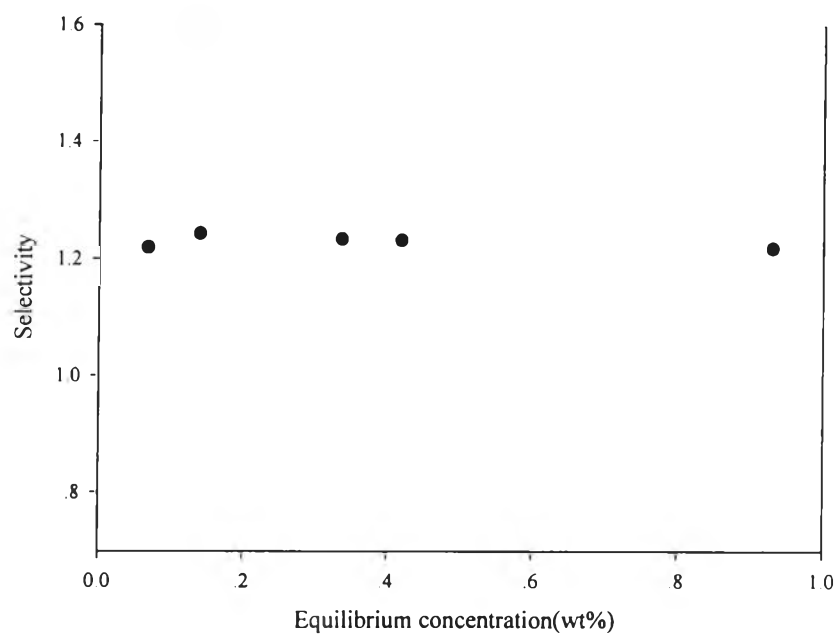


Figure 4.30 Selectivity for n-dodecane/1-dodecene at 25 °C.

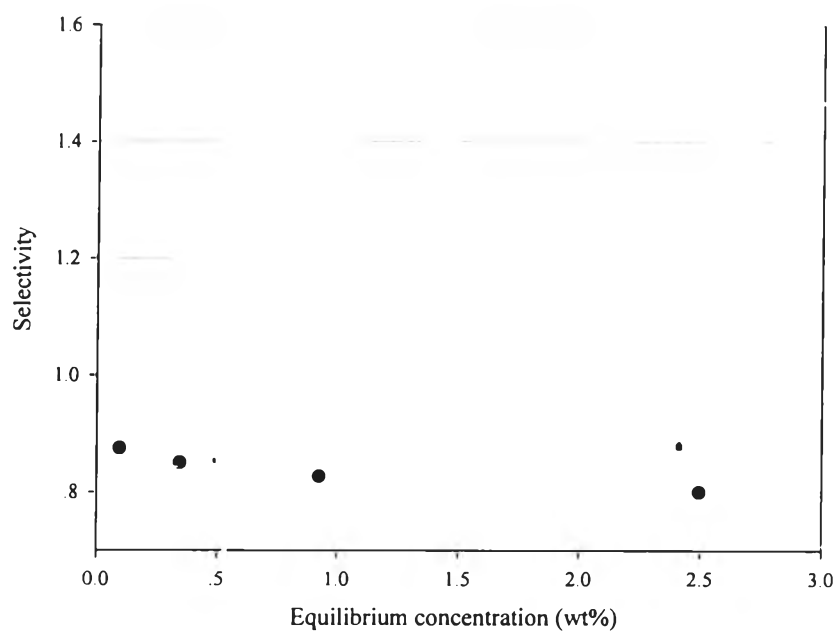


Figure 4.31 Selectivity for n-tetradecane/1-tetradecene at 25 °C.

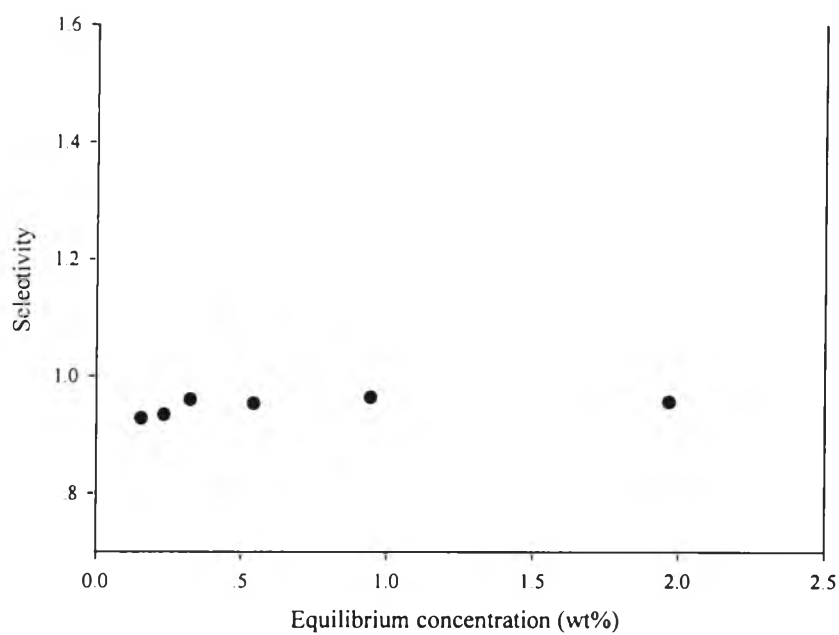


Figure 4.32 Selectivity for n-hexadecane/1-hexadecene at 25 °C.

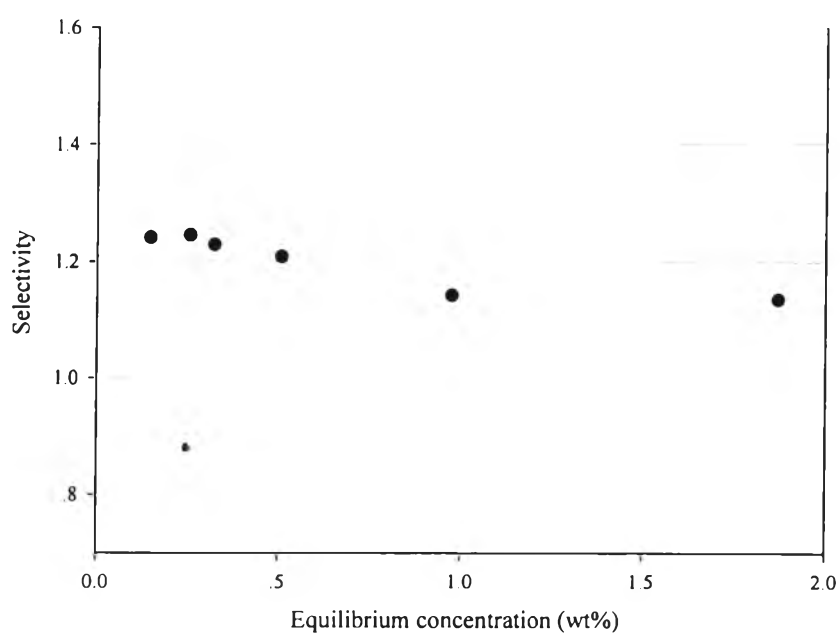


Figure 4.33 Selectivity for n-octadecane/1-octadecene at 25 °C.

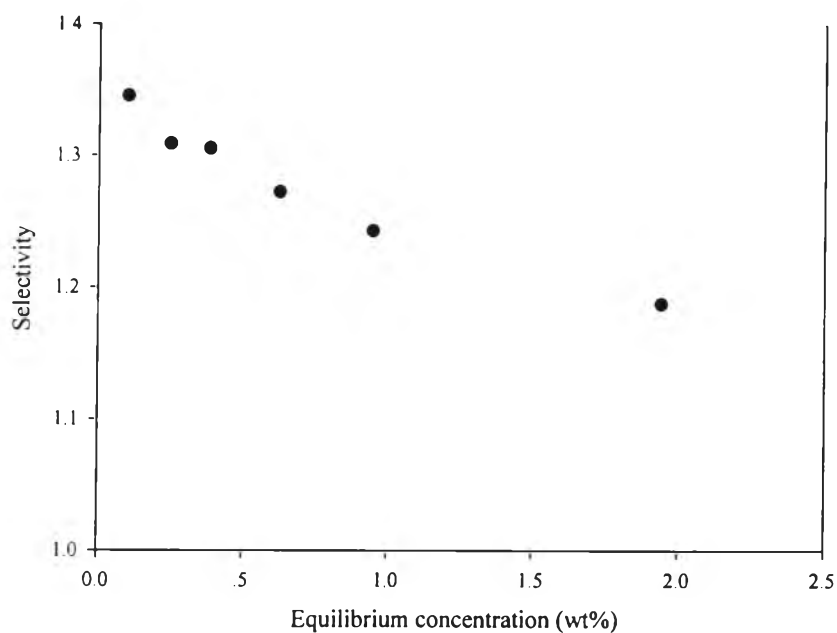


Figure 4.34 Selectivity for n-eicosane/1-eicosene at 25 °C.

Table 4.1 Average equilibrium selectivity for n-paraffin/n-olefin in binary competitive adsorption on silicalite at 25 °C

Mixture	Selectivity
C ₆ /1-C ₆	1.1190
C ₈ /1-C ₈	1.3570
C ₁₀ /1-C ₁₀	1.1460
C ₁₂ /1-C ₁₂	1.2290
C ₁₄ /1-C ₁₄	0.8380
C ₁₆ /1-C ₁₆	0.9490
C ₁₈ /1-C ₁₈	1.2130
C ₂₀ /1-C ₂₀	1.2770

From Table 4.1, the average selectivities for n-paraffin/n-olefin at the same carbon number are close to one. It indicates that, at the equilibrium condition, silicalite cannot be used to separate n-paraffin and n-olefin at the same carbon number.

4.3 Multi-Component Pulse Test Experiments

Besides equilibrium selectivity estimation, pulse test experiments have been performed in order to obtain dynamic selectivity. The pulse test is based on the chromatographic theory. A component that is strongly adsorbed on an adsorbent spends more time in the column (higher net retention volume). On the other hand, a component that does not interact with the adsorbent spends less time in the column (lower net retention volume). More details for the pulse test technique can be found in Appendix A1.2.

4.3.1 Multi-Component Pulse Test: Silicalite Adsorbent

Pulse test results of the feed mixtures between n-paraffin and n-olefin with carbon numbers ranging from 6 to 20 on silicalite at 120 °C are shown in Figures 4.35 to 4.37. Net retention volumes (NRVs) for each component were extracted from the results as shown in Figure 4.38. From Figure 4.38, the NRVs for n-paraffin and n-olefin at the same carbon number are very close to each other, which can be interpreted that, in the dynamic system, silicalite cannot be used to separate n-paraffin and n-olefin at the same carbon number. The dynamic selectivity can be calculated from the ratio between NRVs of n-paraffin and n-olefin at the same carbon number, as shown in Table 4.2, and all the values are close to one.

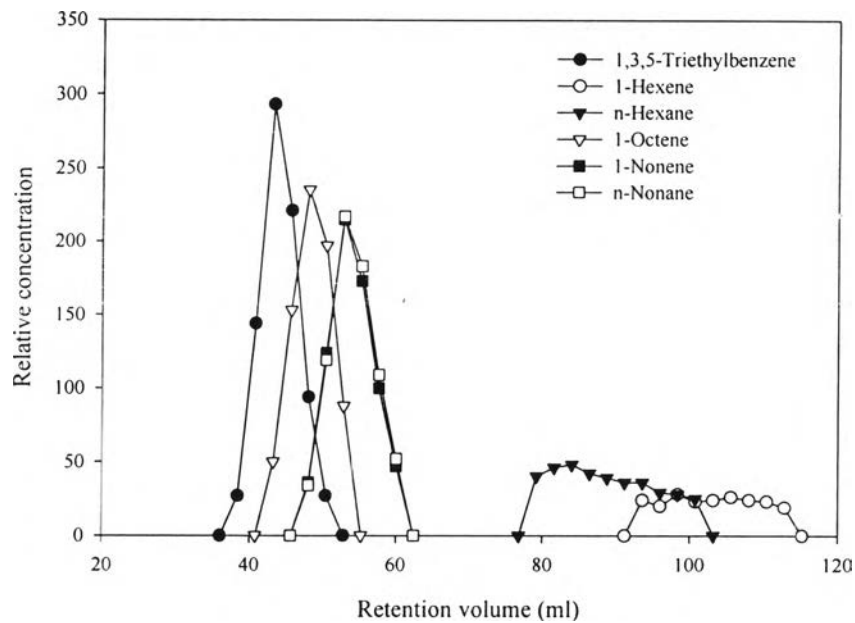


Figure 4.35 Pulse test results for C₆, 1-C₆, 1-C₈, C₉, 1-C₉ on silicalite at 120 °C.

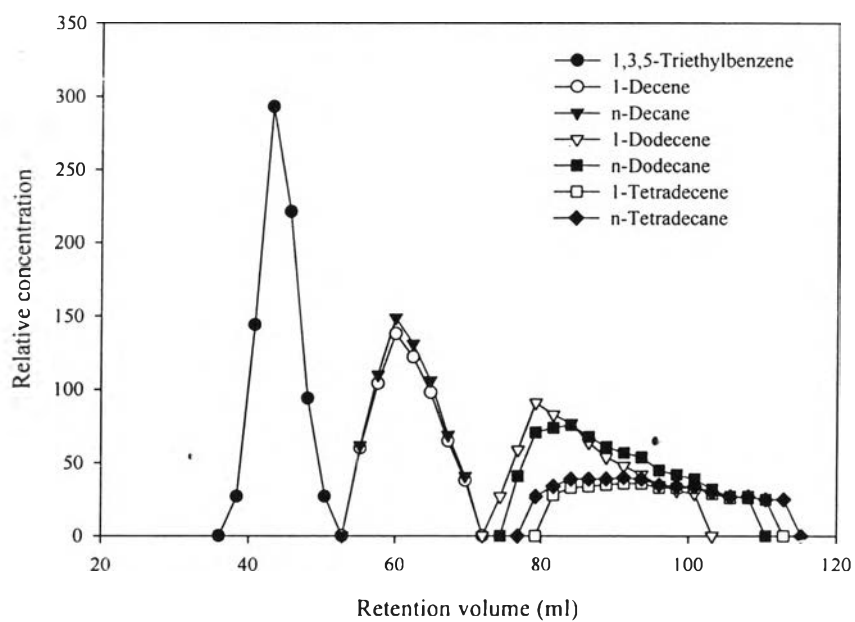


Figure 4.36 Pulse test results for C₁₀, 1-C₁₀, C₁₂, 1-C₁₂, C₁₄, 1-C₁₄ on silicalite at 120 °C.

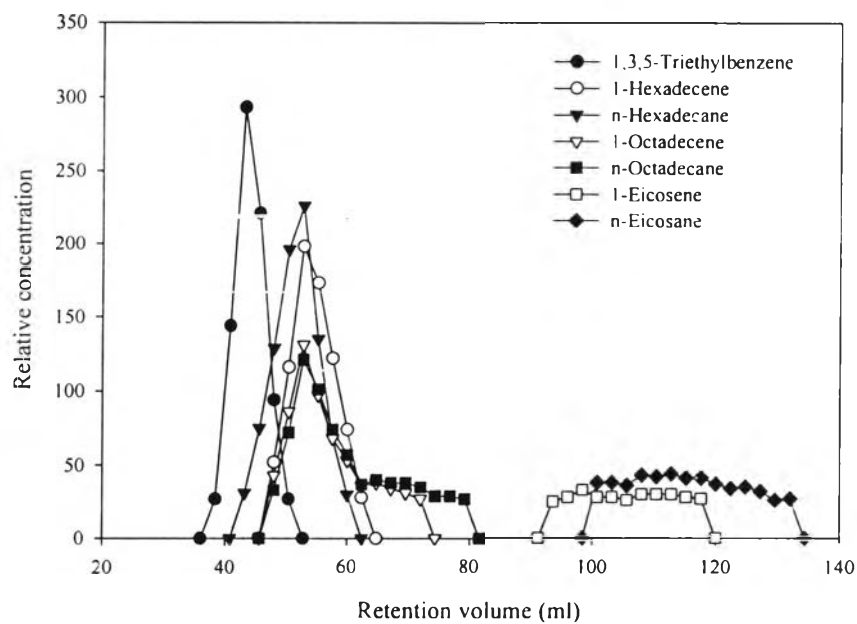


Figure 4.37 Pulse test results for C₁₆, 1-C₁₆, C₁₈, 1-C₁₈, C₂₀, 1-C₂₀ on silicalite at 120 °C.

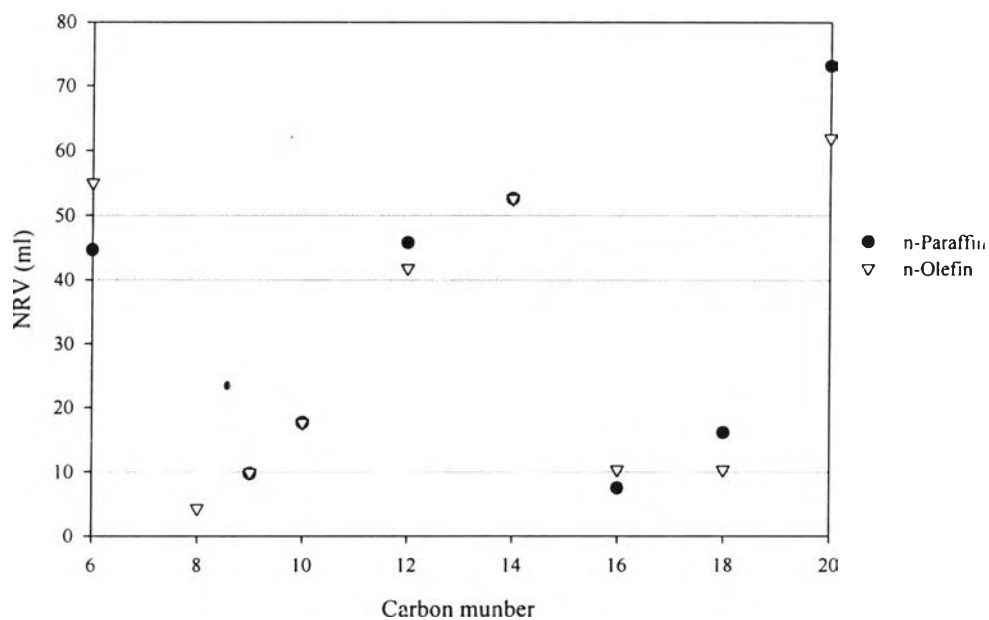


Figure 4.38 Net retention volumes on silicalite for n-paraffin and n-olefin carbon numbers ranging from 6 to 20 at 120 °C.

Table 4.2 Dynamic selectivities for n-paraffin/n-olefin by pulse test method on silicalite at 120 °C

Mixture	Selectivity
C ₆ /1-C ₆	0.8124
C ₉ /1-C ₉	0.9901
C ₁₀ /1-C ₁₀	1.0019
C ₁₂ /1-C ₁₂	1.0954
C ₁₄ /1-C ₁₄	1.0006
C ₁₆ /1-C ₁₆	0.7260
C ₁₈ /1-C ₁₈	1.2256
C ₂₀ /1-C ₂₀	1.1809

Both equilibrium and dynamic selectivities are the same, i.e. silicalite cannot be used to separate n-paraffin and n-olefin at the same carbon number. However, there is a possibility to use silicalite for separation of hydrocarbons with difference carbon numbers.

4.3.2 Multi-Component Pulse Test: NaX Adsorbent

NaX was also tested for the separation of n-paraffin and n-olefin. The same feed composition as previously stated was used with NaX as an adsorbent. Pulse test results are shown in Figures 4.39 to 4.41. NRVs for this system are shown in Figure 4.42. From Figure 4.42, the gap between the NRVs for n-paraffin and n-olefin are obvious indicating that NaX can be used to separate n-paraffin and n-olefin.

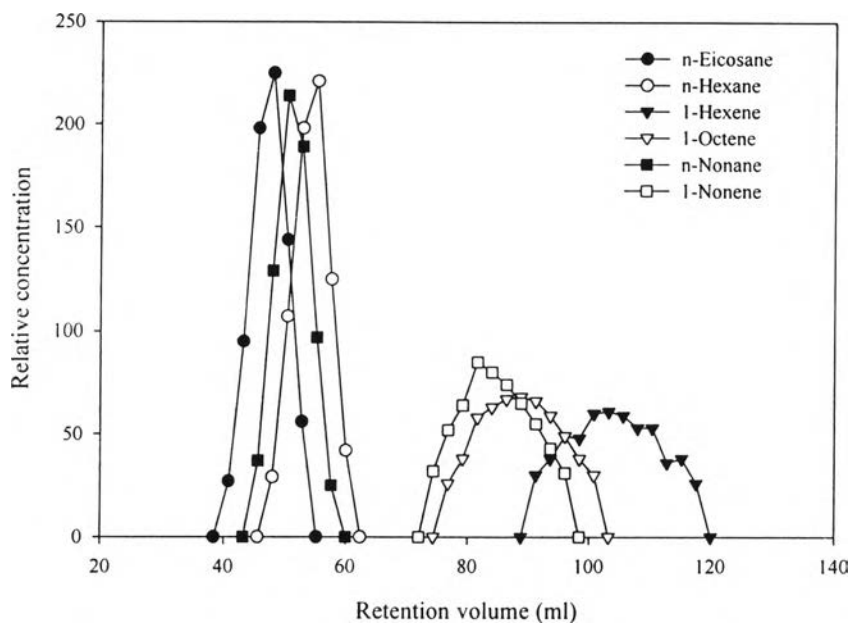


Figure 4.39 Pulse test results for C₆, 1-C₆, 1-C₈, C₉, 1-C₉ on NaX at 120 °C.

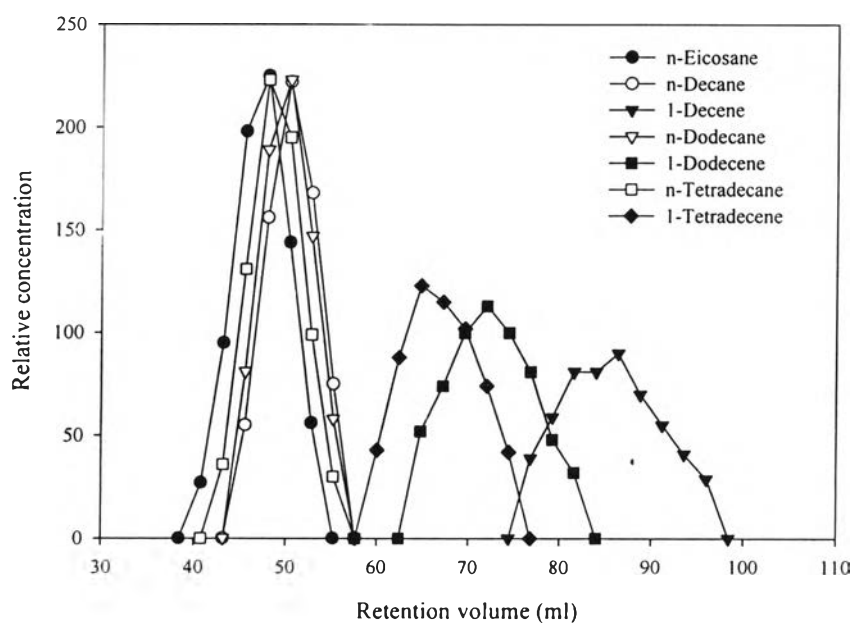


Figure 4.40 Pulse test results for C₁₀, 1-C₁₀, C₁₂, 1-C₁₂, C₁₄, 1-C₁₄ on NaX at 120 °C.

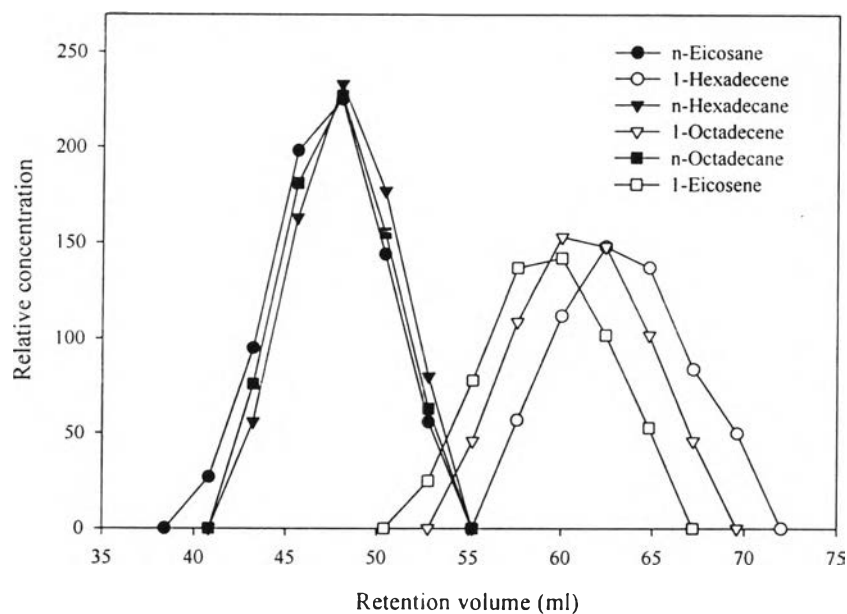


Figure 4.41 Pulse test results for C_{16} , 1- C_{16} , C_{18} , 1- C_{18} , C_{20} , 1- C_{20} on NaX at 120 °C.

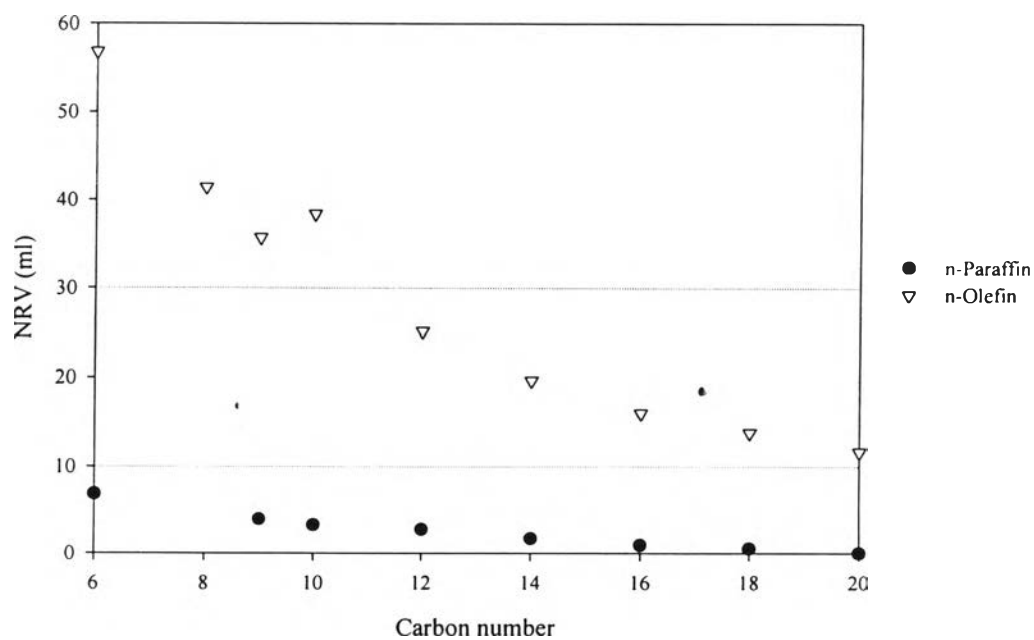


Figure 4.42 Net retention volumes on NaX for n-paraffin and n-olefin carbon numbers ranging from 6 to 20 versus carbon number at 120 °C.

Comparison of dynamic selectivities of n-olefin over n-paraffin using silicalite and NaX from the pulse test experiments at 120°C is shown in Table 4.3. The results show that NaX can separate n-paraffin and n-olefin as it is more selective for n-olefin. This is because of the C=C double bond in olefin molecules makes specific interactions with Na⁺ cations in NaX, whereas n-paraffin lacks of a reactive center to interact sufficiently with the Na⁺ cations (Armaroli *et al.*, 1999). In addition, NaX is more hydrophilic than silicalite, and it is expected to selectively adsorb n-olefin which is more hydrophilic than n-paraffin. Moreover, lewis-acid in NaX are also matching with the molecule that have more basicity like n-olefin than n-paraffin (Kulprathipanja and Johnson, 2001). Silicalite, on the other hand, cannot separate n-paraffin and n-olefin at the same carbon number because of the similar molecular chain length of the n-paraffin and n-olefin.

Table 4.3 Dynamic selectivities for n-olefin/n-paraffin by pulse test method on silicalite and NaX at 120 °C

Mixture	Selectivity on silicalite	Selectivity on NaX
C ₆ /1-C ₆	1.2309	8.2044
C ₉ /1-C ₉	1.0100	9.0296
C ₁₀ /1-C ₁₀	0.9981	11.7265
C ₁₂ /1-C ₁₂	0.9129	9.1362
C ₁₄ /1-C ₁₄	0.9994	11.7636
C ₁₆ /1-C ₁₆	1.3775	17.6031
C ₁₈ /1-C ₁₈	0.6429	27.5987
C ₂₀ /1-C ₂₀	0.8468	-

4.4 Energy Simulation

Adsorption energy for n-paraffin and n-olefin on silicalite was simulated through the straight pore channel of silicalite by using the Solid_Diffusion model in the Accelrys Insight II Molecular Modeling package program. The procedures are as follows. First, a dummy molecule was set up and the silicalite pore channel was constructed with four times longer in length than the dummy molecule. Then, the start and end points were defined in order to direct the molecule move into the design direction, Figure 4.43. Between the start and end points, the distance was divided into interval with 0.25 \AA in length for each interval. The molecule moved into the pore of silicalite step by step. For each step, the adsorption energy was calculated until it reached the lowest energy (error between the loop was less than 0.0001 kcal/mol and 100,000 maximum loops) where the molecule was comfortable in the pore of silicalite. After that, the simulated energy was plotted along with distance between the start and end points, Figure 4.44.

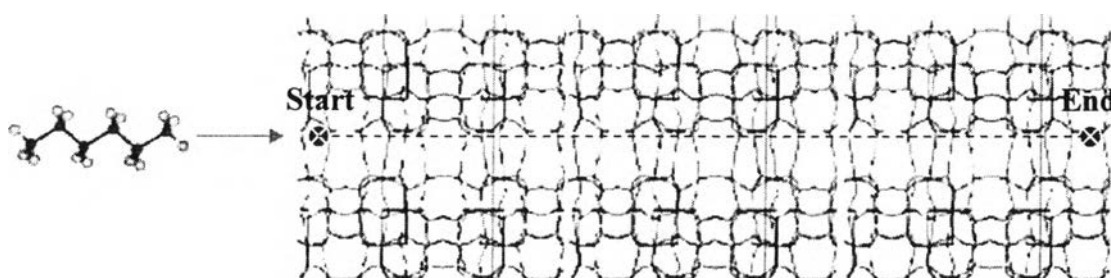


Figure 4.43 Molecule and silicalite pore structure set up for energy simulation.

From Figure 4.44, for all molecules, the energy at the entrance of the channel, 0 to 10 \AA , is higher than that at the position between 10 and 60 \AA . At the beginning of the diffusion, it is difficult for the molecules to penetrate into the pore of silicalite. After that, the molecules move in the pore of silicalite easier as seen from the small difference between the highest and lowest energy from the position of 10 to 60 \AA (less than 8 kcal/mol).

Figure 4.44 shows that relative energy for n-paraffin and n-olefin at the same carbon number is almost at the same energy level. It implies that n-paraffin

and n-olefin at the same carbon number have the similarity in diffusion behavior into the pore of silicalite in the straight channel. In addition, the relative energy decreases with increasing the carbon number, which is attributed to the higher carbon number interaction with the inside pore of silicalite resulting in less adsorption energy.

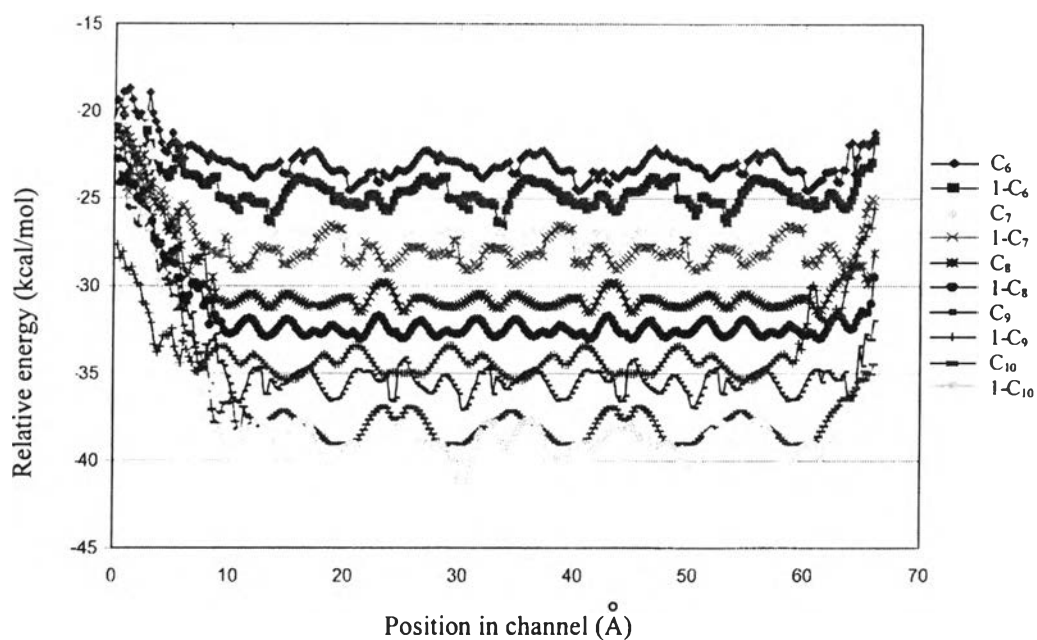


Figure 4.44 Energy simulation for n-paraffin and n-olefin carbon number ranging from 6 to 10.