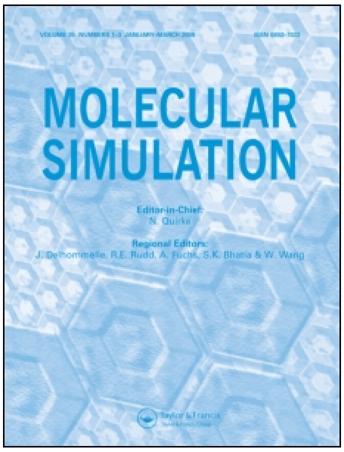

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Behavior of Aromatic Molecules in Silicalite by the Direct Integration of the Configurational Integral

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BEHAVIOR OF AROMATIC MOLECULES IN SILICALITE BY THE DIRECT INTEGRATION OF THE CONFIGURATIONAL INTEGRAL

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Adsorption data of aromatic molecules adsorbed in silicalite show highly unusual characteristics which were attributed to structural effects caused by the comparable size of molecules and pores. In this study, the interaction of aromatic compounds with silicalite are examined on the molecular level. The interactions are calculated by atom–atom approximation using Lennard-Jones potentials. The constants are calculated, without fitting, from Kirkwood–Muller formulas. Benzene and p-xylene are represented as a rigid structure of 12 and 18 atom centers. The model is anisotropic.

The diffusional behavior of molecules is examined by minimizing the potential energy in the channels which requires less computational time than Molecular Dynamics. The activation energy for the diffusion of benzene, 27.6 kJ/mol, is in excellent agreement with data, 28.8 kJ/mol. The results indicate that both molecules can enter the smaller zig-zag channels. The energetically most favorable location in the main channels is the mid-point between intersections. All rotations are restricted in the channels but the molecules can rotate in any direction (with some movement of the center) at intersections.

The Henry's law constant and internal energy of adsorption at zero coverage are calculated by direct integration of the configurational integral. Direct integration is more efficient than Monte Carlo and Molecular Dynamics simulations since the molecules are highly restricted in the pores. The predicted internal energy of adsorption, −54.86 and −75.30 kJ/mol for benzene and p-xylene is in good agreement with data of −50.92 and −62.15 kJ/mol respectively. There is appreciable difference between the predicted and experimental Henry's law constants. The agreement can be improved by fitting the Lennard-Jones constants which has not been attempted.

Although the calculations are performed at infinite dilution and entropy effects are not included, the results bring insight to the behavior of molecules in highly restricted environments such as in tight pores. Similar simplified calculations can be used to close the gap between highly idealized molecular simulations and complicated systems common in real applications.

KEY WORDS: Silicalite, benzene, p-xylene, adsorption, activation energy.

1 INTRODUCTION

Adsorption data for aromatic compounds in silicalite show highly unusual characteristics such as steps in the isotherms at moderate loadings [11, 4] and extremes in the heat of adsorption [13]. These unusual characteristics have been attributed to structural effects caused by the comparable sizes of molecules and silicalite pores. These systems are examined at a molecular level in this study in order to better understand these structural effects.

The aromatic molecules are very restricted in the silicalite pore structure. Traditional molecular simulations such as Monte Carlo and Molecular Dynamics may not be computationally feasible to study these systems. The success ratio is very low in Monte Carlo simulations and the time step needs to be extremely small in Molecular Dynamics. Both approaches would require considerable computational time in order to yield any meaningful result. In this study, the thermodynamic properties are calculated by the direct integration of the configurational integral following the approach used by Bezus *et al.* [1]. The diffusional properties which are normally deduced from Molecular Dynamic simulations are calculated by a hybrid approach based on minimizing the potential energy similar to the study by Pickett *et al.* [9]. As will be shown, molecular insight can be gained, although not as complete as from Molecular Dynamics, by these methods which has great computational time advantages.

2 STRUCTURE OF SILICALITE

Silicalite is a pentasil zeolite. It consists of pure crystalline silica. It does not contain any alumina, thus there cannot be any cations present in the structure. The unit cell contains 96 silicon tetrahedra [3]. Crossections of silicalite crystal, benzene and p-xylene molecules are shown in scale in Figure 1. The unit cell dimensions are $a = 19.961$ Å, $b = 19.824$ Å and $c = 13.398$ Å [12]. The crystal has $Pn2_1$ space group corresponding to a 8-fold symmetry in the unit cell.

The pores of silicalite are formed by 10-membered oxygen rings. There are two interconnected channels in silicalite; straight "main" channels with elliptical crossection of about 5.7 × 5.1 Å in the *b*-direction running throughout the unit cell, and zig-zag "side" channels with circular crossection of about 5.4 Å diameter in the *a*–*c* plane. Each unit cell contains 2 main channels and 4 side channels.

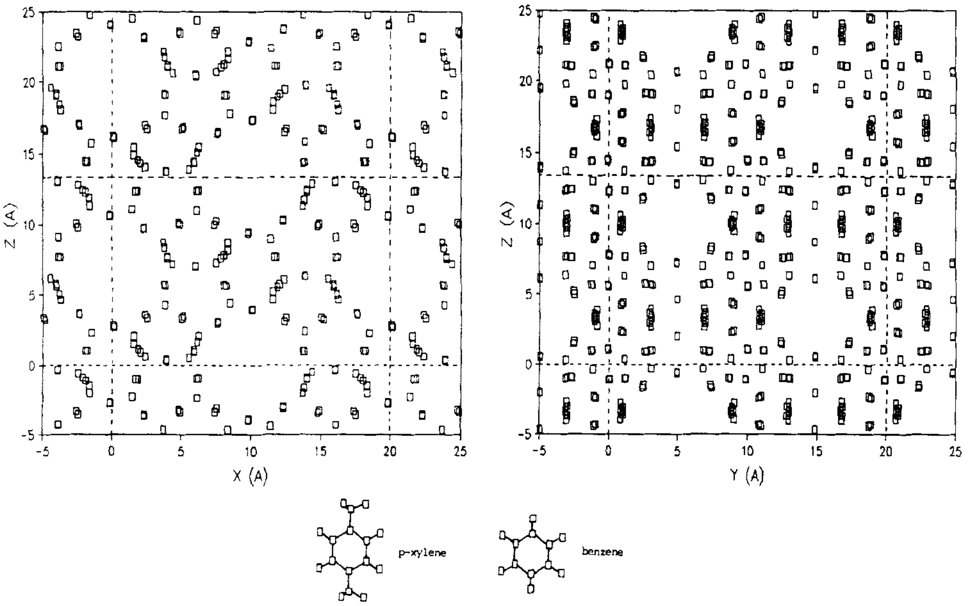

Figure 1 Silicalite crystal and aromatic molecules (in scale).

3 ATOM-ATOM APPROXIMATION

An Atom–Atom Approximation (AAP) is used in the calculation of vertical interactions. In this approach, the total interaction potential, ϕ_{tot}, of a molecule with the solid is represented as

$$\phi_{\mathrm{tot}} = \sum_i \sum_j \phi_{ij} \tag{1}$$

where ϕ_{ij} is the interaction potential between the ith atom on the molecule and the jth atom on the solid.

The silicalite crystal is represented by 192 oxygen atoms in a unit cell. The silicon atoms are neglected; their interactions are effectively lumped into the oxygen interaction constants. The oxygen locations are taken from Taylor [12]. All oxygen atoms within a 20 Å radius are considered in the simulations. This results in about 1200 atoms for the summation on the solid in Equation (1). The total potential is not corrected for the effect of atoms beyond 20 Å. This represents less than a 0.5% contribution to the total potential.

The locations of carbon and hydrogen atoms in benzene molecule were fixed; benzene molecule is a rigid structure. Although there is rotational freedom of the methyl groups in p-xylene, this is ignored since the hydrogen atoms are small and the change in their position by rotation is also small. Effectively, p-xylene is also treated as a rigid structure. The summation over atoms in molecules in Equation (1) considers 12 atoms for benzene and 18 for p-xylene.

The AAP is an ansiotropic formulation. The position of molecules are expressed by a vector consisting of 3 cartesian coordinates (x, y, z) showing the center of the molecule, and 3 Euler angles (Φ, Θ, Ψ) showing the orientation of the molecule. The coordinate system is fixed on the solid structure and the location of each atom in the molecule are calculated with the given position vector.

4 POTENTIAL ENERGY FUNCTION

Lennard-Jones potential energy function is used to describe the interaction between atom pairs.

$$\phi_{ij} = \frac{B_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \tag{2}$$

The attractive constant, C_{ij}, is calculated following the Kirkwood-Muller approach [5, 7].

$$C_{ij} = \tfrac{3}{2}e^2\sqrt{a_0}\cdot\frac{\alpha_1\alpha_2}{\sqrt{\frac{\alpha_1}{n_1}} + \sqrt{\frac{\alpha_2}{n_2}}} \tag{3}$$

The repulsive constant, B_{ij}, is calculated from the condition of minimum potential at the equilibrium interatomic distance equal to the sum of the Van der Waals radii of interacting atoms.

$$B_{ij} = \tfrac{1}{2}C_{ij}(r_i + r_j)^6 \tag{4}$$

The atomic radii are taken from Bondi [2].

Table 1 Lennard-Jones potential constants for atom pairs.

Atom	*Polarizability (1000 cu · nm)*	*Radius (A)*	*Atom Pair*	*C (kJ · A/mol)*	*B (kJ · A/mol)*
O	0.85	1.52	C-O	0.2157×10^4	0.1444×10^7
H	0.40	1.35	H-O	0.5364×10^3	0.1499×10^6
C	1.34	1.80			

All relevant information for the calculation of L-J constants are listed in Table 1. It should be noted that the potential energy function constants are predicted in this work. Data was not used to optimize the values of these constants. Results discussed in this paper are calculated *a priori*; they can be improved by fitting the L-J constants to available data.

5 MINIMIZED POTENTIALS AND DIFFUSION

The diffusion of molecules in the channels is investigated by minimizing the potential energy. In a similar fashion to the study by Pickett *et al.* [9], the molecule is shifted along the channel axis at 0.1 Å steps, and at each step the potential energy is minimized by allowing movement along the two remaining axes and rotation around all three axes. A typical calculation minimizing around 100 steps takes about 30 min CPU time on a VAX 8650 computer.

The minimization routine is expected to give a better estimate of the energy path during diffusion than that could be obtained from energy contour maps used by Kiselev *et al.* [6]. Results discussed here refer to a hypothetical case of diffusion at absolute zero temperature, where the molecules follow the minimum energy path. At higher temperatures, a molecule is no longer restricted to the minimum energy path due to the increased kinetic energy.

5.1 *Main Channel*

Figure 2 shows the minimized potentials in the main channel. The potentials are symmetric around $Y = 0$ due to the silicalite crystal symmetry. As expected, the p-xylene interaction is about 25–30 kJ/mol stronger than benzene interaction. The two curves for the two molecules are amazingly similar with only a shift in the total potential. The global minimum potential is -68.2 kJ/mol for benzene and -90.1 kJ/mol p-xylene occuring at the middle of the channel.

There are two other local minima; one at the channel intersections and a second at about 1/4'th distance into the main channel. The distances between these locations is about 2.5 Å which renders them mutually exclusive if the size of aromatic ring (about 6 Å) is considered. In other words, if a benzene molecule is located at the global minimum, another one cannot fit into the adjacent local minima locations. However, there is a chance that molecules can be located at the global minimum and also at the channel intersections simultaneously, since there is a lot of freedom for movement at the channel intersections.

Previous studies suggested that the benzene molecules are most favorably located at the channel intersections for the sister zeolite, ZSM-5 [8]. Our results show that the most favorable location is the mid point between channel intersections. The difference

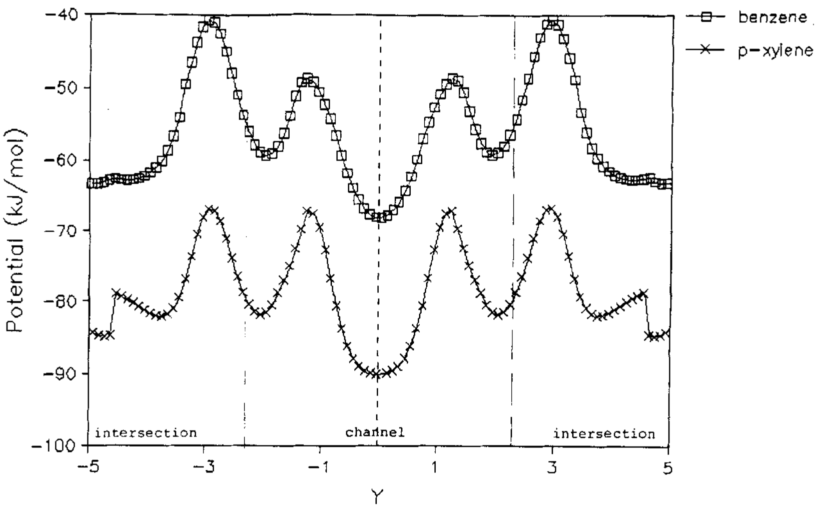

Figure 2 Minimized potentials in the silicalite main channel.

might be caused by the alumina atoms in the ZSM-5 structure. In addition, results presented here are exact only if the kinetic energy of the molecules are zero. At normal temperatures, the increased mobility of molecules may prevent them from staying at the mid point where the molecules are very restricted.

The activation energy for diffusion in the main channels can be approximated by differencing the minimum and maximum potential energies. The predicted activation energy is 27.6 kJ/mol for benzene. Pickett *et al.* [9] predict about 25 kJ/mol for benzene which is close to our result. Our results agree very well with the available experimental data of 28.8 kJ/mol by Shah *et al.* [10]. Experimental data by Wu *et al.* [14] suggests 21 kJ/mol. The agreement supports the usefulness of the simulation method used in this study. Normally, the activation energies are derived from molecular dynamics studies which require orders of magnitude more computations. The predicted activation energy for p-xylene is 23.3 kJ/mol. Data is not available for comparison.

Figure 3 shows the movement of benzene in the main channel in X–Y plane. At the intersections, benzene molecule is almost completely in X–Y plane, and it prefers to be located closer to the side channel opening rather than at the center. As the molecule moves into the main channel, it tilts around the Z-axis. Complete rotations perpendicular to the aromatic ring is not possible in the main channels. In agreement with our previous speculations [11], the aromatic ring cannot rotate in the channels. Figure 4 shows the same movement in X–Z plane. Benzene stays very close to the center of the main channel as it moves through the main channel. At the intersections, the aromatic ring is perpendicular to the X–Z plane.

Figures 5 and 6 show the movement of p-xylene in the main channel. Similar to benzene, p-xylene is also almost completely in the X–Y plane at channel intersections, and it prefers to be located closer to the side channel opening. As it moves into the main channel, p-xylene also tilts around the Z-axis. As expected, the methyl groups point in the direction of channel axis. They are closer to the channel wall since the total interactions are larger due to the reduced distance of the methyl groups from

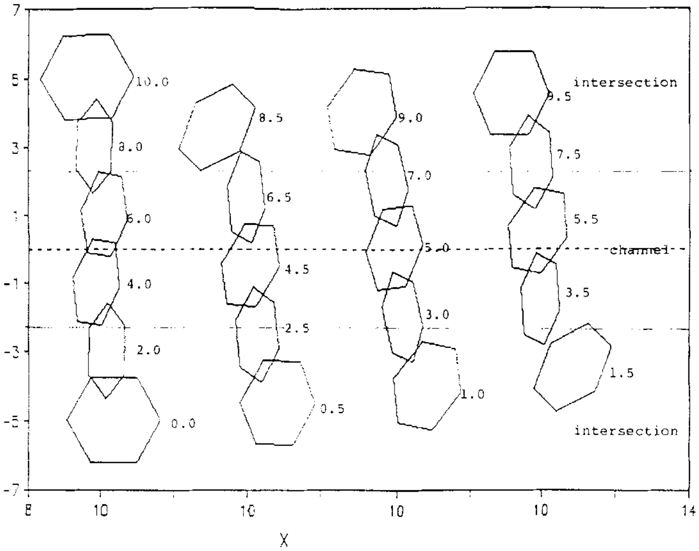

Figure 3 Benzene X-Y projections in silicalite main channel.

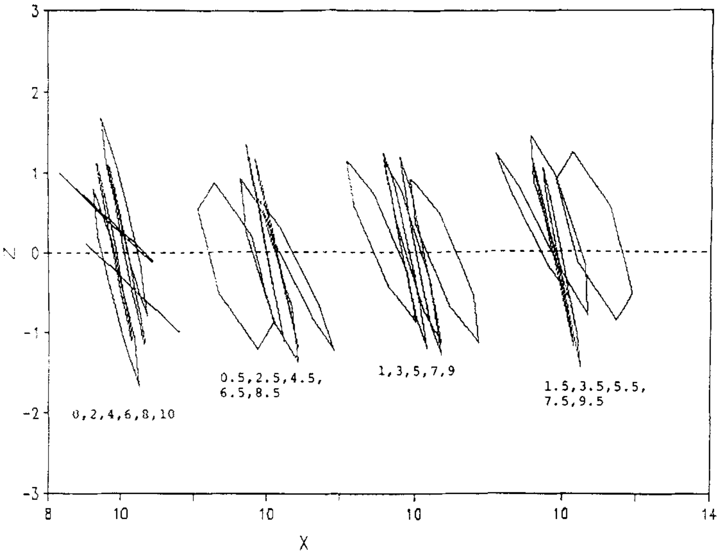

Figure 4 Benzene X-Z projections in silicalite main channel.

wall atoms. p-Xylene also cannot rotate around the aromatic ring in the channels due to the existence of methyl groups.

5.2 *Side Channel*

Figure 7 shows minimized potentials as the molecules move through the side channels from intersection to intersection. There is no symmetry in these potentials since the

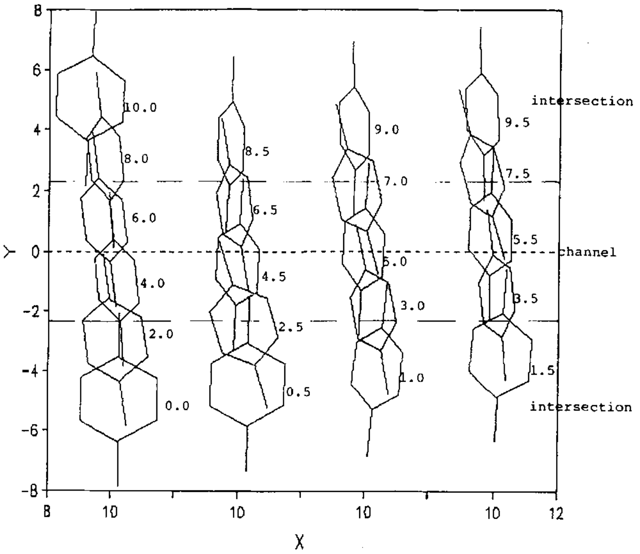

Figure 5 p-Xylene X-Y projections in silicalite main channel.

side channels are asymmetrical. Both molecules can enter the side channels as indicated by the negative potentials. The minimum potential for benzene is −68 5 kJ/mol occuring mid-way between intersections which is comparable to −68.2 kJ/mol found for benzene in the main channels. There are several other local minima. These locations are mutually exclusive due to the size of the aromatic ring. The potential barrier that benzene has to overcome to enter a side channel from one

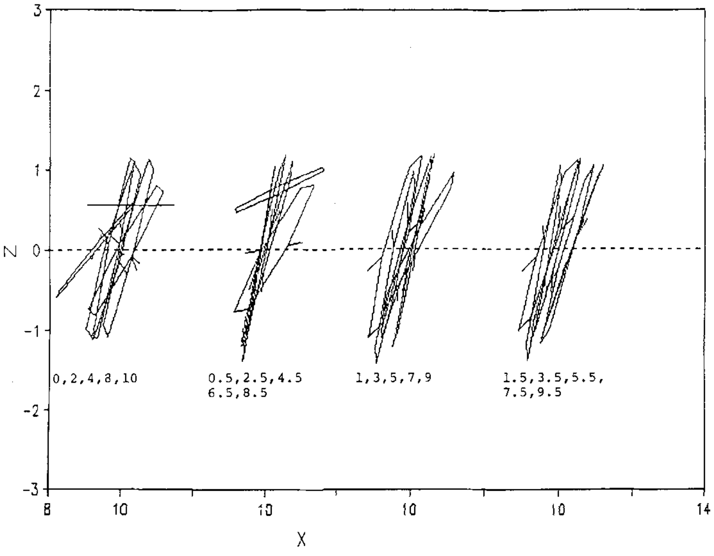

Figure 6 p-Xylene X-Z projections in silicalite main channel.

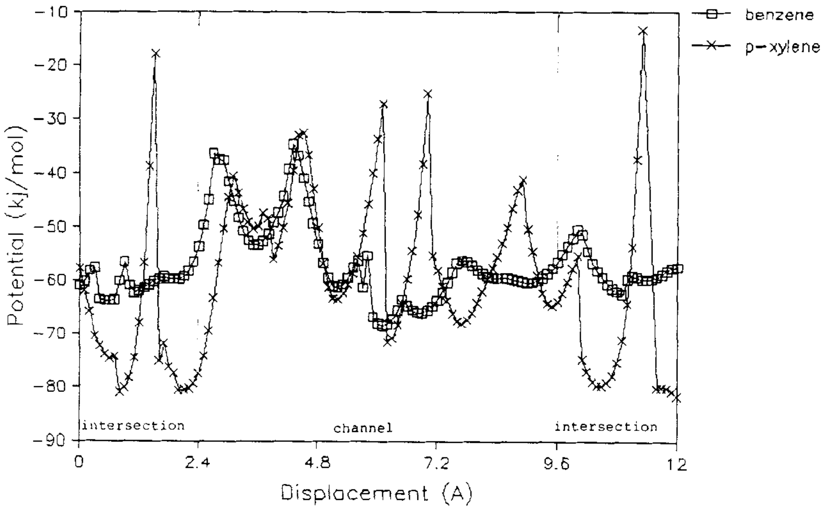

Figure 7 Minimized potentials in silicalite side channel.

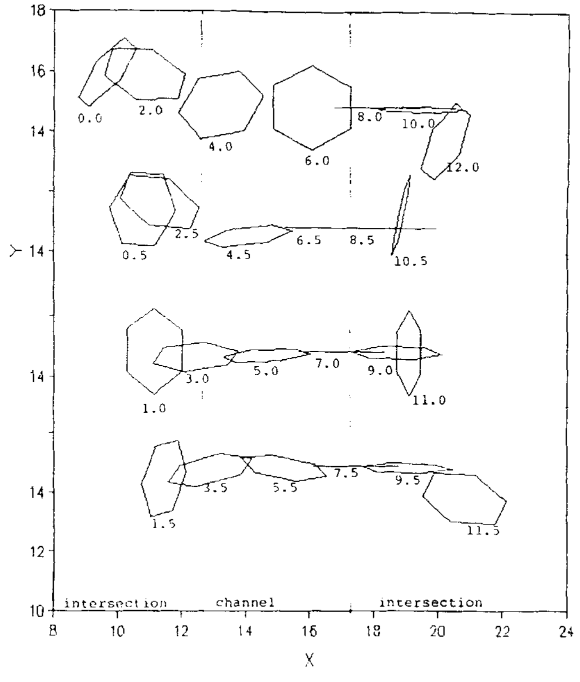

Figure 8 Benzene X-Y projections in silicalite side channel.

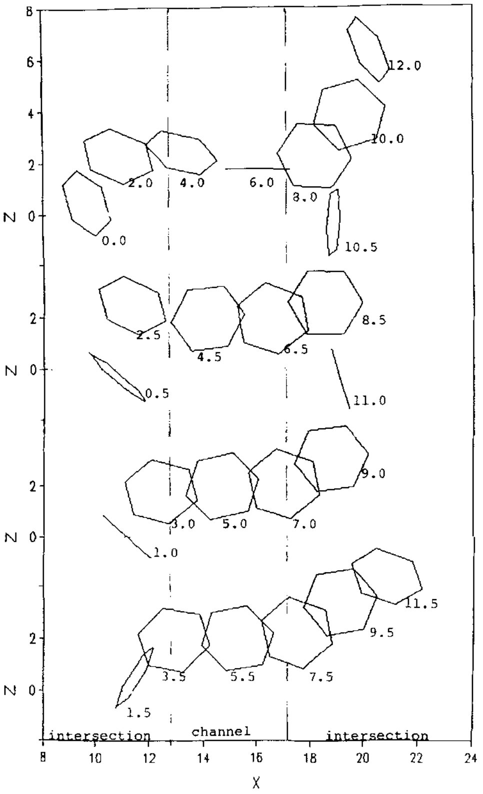

Figure 9 Benzene X–Z projections in silicalite side channel.

side is about 25 kJ/mol, while from the other side is about 10 kJ/mol. In other words, benzene can enter the side channel easier from one side than the other side. This is an important finding caused by the asymmetry of the crystal around the side channels.

Figures 8 and 9 show the projection of benzene molecule on X–Y and X–Z planes as it travels through the side channels. As apparent in the figures, benzene can be completely contained in the side channels. It is interesting to note that the molecule is completely in the X–Y plane where the minimum occurs. The benzene molecule has to re-orient in order to arrive at this position. The difference between the energy barriers approaching the minimum energy location from the two sides is probably caused by the difference in the ease of this re-orientation. The benzene has to go through a 90 degree turn in 0.5 Å distance in order to reach at the minimum potential point, and immediately go through another 90 degree turn in order to continue to move. The p-xylene molecule has a much more complicated behaviour than benzene in the side channels. The potential barrier for diffusion is about 70 kJ/mol, and it is about same at both ends of the side channel, Figure 7. There is a sharp minimum at the middle of the channel similar to benzene. As can be seen in Figures 10 and 11, the p-xylene has to go through a drastic re-orientation before entering the side channel. In both the side and main channels, the methyl groups are parallel to the channel axis,

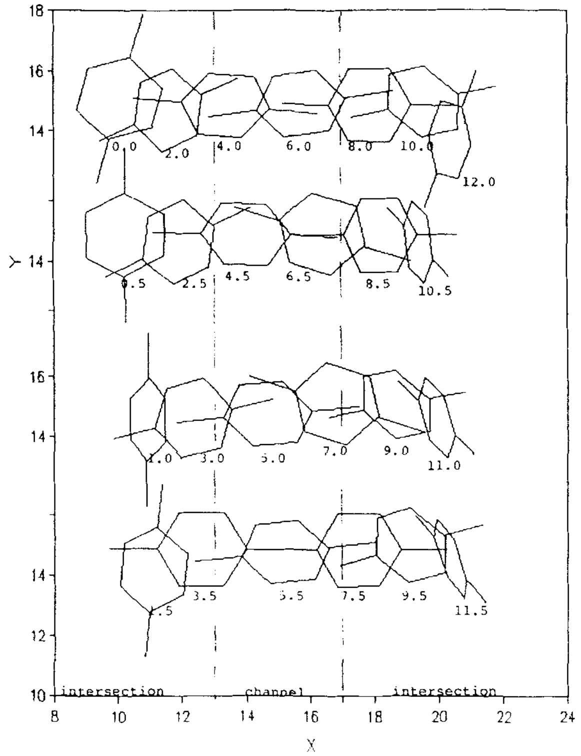

Figure 10 p-Xylene X–Y projections in silicalite side channel.

which implies a 90 degree turn before entering the side channel. Unlike benzene, this re-orientation occurs in the intersections where more space is available. Another difference between benzene and p-xylene is that p-xylene cannot be completely contained in the side channels.

6 THERMODYNAMIC PROPERTIES

The Henry's Law constant and internal energy of adsorption at zero coverage (infinite dilution) are calculated by direct integration of the configurational integral [1]. The Henry's law constant is given by;

$$K = \frac{1}{8\pi^2 Vd} \int_r \left[\exp\left(- \frac{\phi_{\mathrm{tot}}}{\mathrm{RT}} \right) - 1 \right] \mathrm{d}r \tag{5}$$

where V is the integration volume ϕ_{tot} is the total interaction potential and $d = 1.8048\,\mathrm{gm/cm^3}$ is the silicalite density. The position vector, r, consists of six entries, three cartesian coordinates for the center of the molecule and three Euler's angles describing the orientation of the molecule. The internal energy of adsorption is the

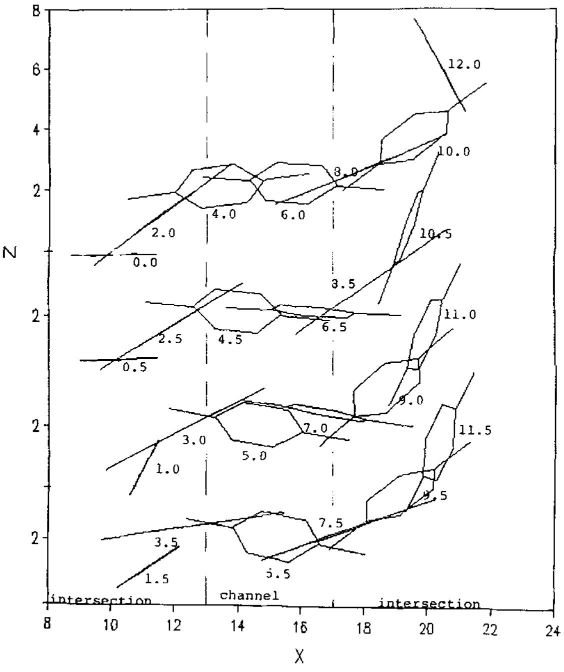

Figure 11 p-Xylene X-Z projections in silicalite side channel.

first derivative of the Henry's law constant with respect to temperature.

$$\Delta U = \frac{\int_r \phi_{\text{tot}} \exp\left(-\frac{\phi_{\text{tot}}}{RT}\right) \mathrm{d}r}{\int_r \left[\exp\left(-\frac{\phi_{\text{tot}}}{RT}\right) - 1\right] \mathrm{d}r} \tag{6}$$

The above integrations were carried out on a 0.5 Å grid superimposed on the silicalite crystal. First the sum of inverse 6'th and 12'th powers of distances for every oxygen atom within 20 Å were calculated and stored in a large array. If any oxygen atom was closer then 1.9 Å to a grid point, that point was omitted because the repulsive part of the potential energy would overwhelm the attractive part resulting in negligible contribution to the integrals. Generation of the grid took about 20 min CPU time on a VAX 8650 mainframe computer. The integration volume was 1/8'th of a unit cell corresponding to the smallest asymmetrical volume ($0.0 < X < 0.5$, $0.0 < Y < 0.25$, $0.0 < Z < 1.0$).

For the calculation of real potentials, the center of molecules are moved over the grid. At every grid location, a sufficiently small step in Euler's angles are taken in order that the movement of the furthest atom from the molecular center is 0.5 Å (grid increment). The total potential is calculated by summing over all atoms on the molecule utilizing the previously stored summations over solid atoms. The integrations are performed by the Simpson's Rule. Calculation of integrals took about 40 min CPU time on a VAX 8650 computer for benzene.

A 0.5 Å grid may seem to be rather coarse for the systems studied. Figure 12 shows the Euler's angle averaged potential at $X = 0.0$ for several Y values as a function Z

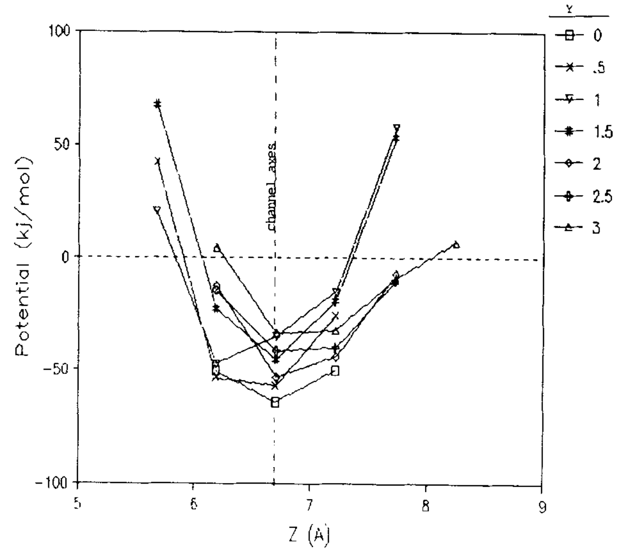

Figure 12 Angle averaged potential energy of benzene in silicalite main channel at grid points (X = 0.0).

in the main channel. The entire abcissa in the figure is actually contained within the main channel which shows how much benzene is restricted in the channels. Only 1 Å movement in Z direction results in a "wall collision" and the potentials sharply increase to positive values. Although the potential wells are very sharp, at least three locations show attractive energies at each crossection. Figure 13 shows the angle

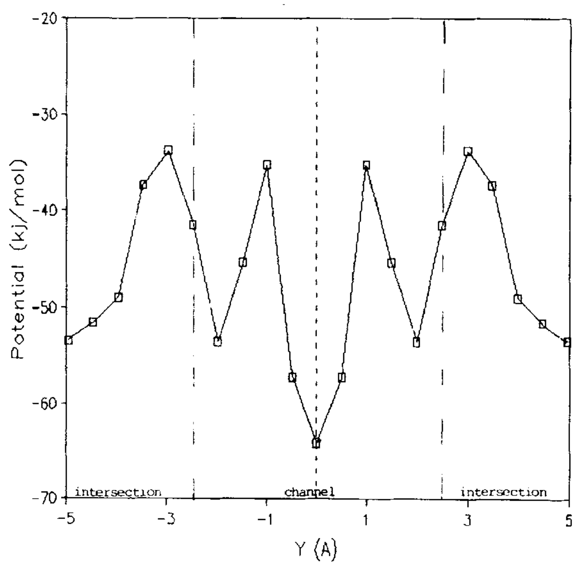

Figure 13 Angle averaged potential energy of benzene along main channel axes at grid points (X = 0.0, Z = c/2).

averaged potential along the channel axis. Compared to Figure 2, it can be seen that most of the essential features of minimized potentials are captured by this rather coarse grid.

The Henry's Law constant calculated from Equation (5) is 2.025 × 10^6 cm^3/gm for benzene at 20°C. The experimental result is 0.1247 × 10^6 cm^3/gm [11]. The difference between experimental results and the calculated value is quite large. Although some of this difference can be explained by the inaccuracy in experimental results caused by the very steep isotherms at the origin, some blame must be placed on the simulation results. Either the grid is to coarse or the predicted L–J constants are not accurate enough. We think that the grid is not too coarse especially since the internal energy of adsorption determined from simulations, − 54.86 kJ/mol is in quite good agreement with the experimental result of − 50.92 kJ/mol. The L–J constants can, of course, be determined from experimental results to give a better agreement, but that would defeat the purpose of this study.

The Henry's Law constant from simulations is 224.34 × 10^6 cm^3/gm for p-xylene at 20°C while the experimental value is 0.623 × 10^6 cm^3/gm. The difference in this case is unacceptable. The internal energy of adsorption for p-xylene is − 75.30 kJ/mol from simulations and − 62.15 kJ/mol from experiments. Once again, the internal energies are in reasonable agreement while the Henry's Law constants differ appreciably.

7 CONCLUSIONS

Aspects of the diffusional behavior of molecules in solids can be deduced from minimized potential energies as shown in this study for aromatic molecules in silicalite. This approach is faster than Molecular Dynamics simulations. These systems are very demanding because the molecular sizes are very close to pore sizes. The validity of minimization approach needs to be checked against other systems.

It is shown that both benzene and p-xylene can enter the side channels in silicalite. The activation energy for diffusion is predicted to be 27.6 kJ/mol for benzene which is in excellent agreement with experimental data of 28.8 kJ/mol. The activation energy for p-xylene is predicted to be 23.3 kJ/mol. The molecular behavior in the main and side channels were as expected; the aromatic ring cannot rotate in the channels while even the p-xylene can rotate in the intersections. It is also shown that the p-xylene methyl groups sweep close to the channel walls as it travels through the main channels.

The thermodynamic properties were calculated by direct integration of the configurational integral. The internal energy of adsorption at zero coverage, − 54.87 and − 75.30 kJ/mol for benzene and p-xylene, are in good agreement with experimental data, − 50.92 and − 62.15 kJ/mol respectively. The Henry's Law constants are appreciably different than experimental results. Data can be used to optimize the L–J constants for a better agreement, but that would defeat the purpose of an *a priori* prediction attempted in this study.

Computationally, the direct integration of configurational integrals requires much shorter time than Monte Carlo and Molecular Dynamics simulations especially for the rather coarse integration grid used in this study. On the other hand, the Henry's Law constants are not predicted accurately enough. It is not possible to identify the cause of the inaccuracy. It can be caused either by the coarse grid or by the inaccurate L–J constants. If a finer grid is necessary for more accurate results, the computational advantage might disappear; the computational time roughly increases with the sixth power of number of increments. Improving the L–J constants requires either data fitting or better approximations than the Kirkwood–Muller approach.

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