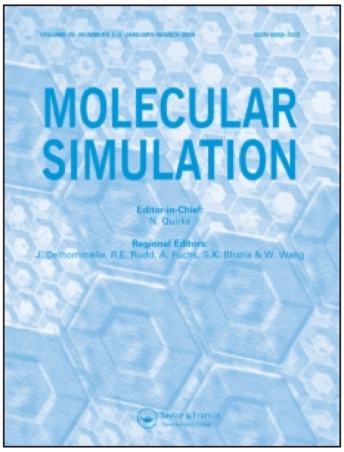

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A COMPUTER SIMULATION OF THE ADSORPTION AND DIFFUSION OF BENZENE AND TOLUENE IN THE ZEOLITES THETA-1 AND SILICALITE

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The influence of the framework geometries of zeolites on the adsorption and diffusion of benzene and toluene molecules has been studied through computer simulations. The behaviours of the uni- and bi-dimensional pore zeolites, theta-1 and silicalite, respectively, have been compared.

KEY WORDS: Zeolite, benzene, toluene, interaction energy, heat of adsorption, activation energy of diffusion.

INTRODUCTION

Zeolites are crystalline aluminosilicates whose three-dimensional frameworks consist of corner-sharing SiO_4 and AlO_4 tetrahedra. Their uniqueness lies in the resulting intra-crystalline channels and cages that are responsible for the shape-selectivity (at the molecular level) exhibited by a number of these materials. Theta-1 is reported [1] to be the first uni-dimensional medium pore (with a radius of 5.5 Å), high-silica zeolite with 10 T-rings (T = Si or Al). These are interlinked along the c-axis direction at a 5 Å repeat (see Figure 1). Silicalite, which is isomorphous with another zeolite, ZSM-5, differing only in the Al content, also has 10 T-rings (see Figure 2). Thus, the pore structures of both theta-1 and silicalite [2, 3] have sets of straight, near-circular channels of similar dimensions. Silicalite, however, has a second set of sinusoidal channels (with a varying radius of 5.1 to 5.4 Å), also consisting of 10 T-rings, intersecting the straight channels to create cage-like pores of nearly 9 Å diameter.

The shape-selectivity of the two zeolites can be judged by the ratios of the products formed during the methylation reaction of toluene with methanol. Catalysts that show no initial shape-selectivity produce xylene isomers in proportions close to the equilibrium mixture: *para*:*meta*:*ortho* = 24:52:24 % weight. Shape selective zeolites yield a higher proportion of *para*-xylene than 24%, presumably because *para*-xylene is more mobile in the zeolite than the *ortho*- and *meta*-isomers, and can readily pass

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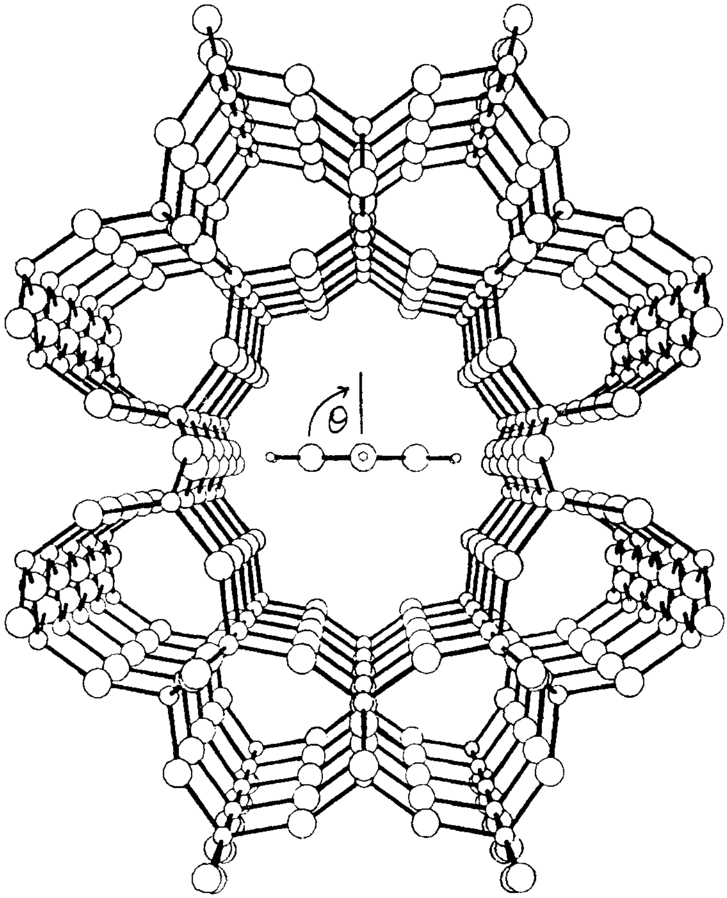

Figure 1 The channel axis projection of benzene in theta-1 in its initial configuration. In the "parallel" movement, the molecule is allowed to rotate about its long molecular axis, which is parallel to the channel axis.

out of the catalyst. The theta-1 catalyst has been shown to have high selectivity [4] for *p*-xylene production. Silicalite, on the other hand, is less selective because of the large cage-like intersections. In this paper we aim to bring out these subtle influences of the structures of adsorbates and zeolites by studying the energetics of benzene and toluene as a function of their orientations and displacements along the straight channels of the two zeolites.

INTERATOMIC POTENTIALS

In calculating the interactions between the adsorbate molecules and the zeolite framework, we employ the Lennard-Jones description of the atom–atom potentials:

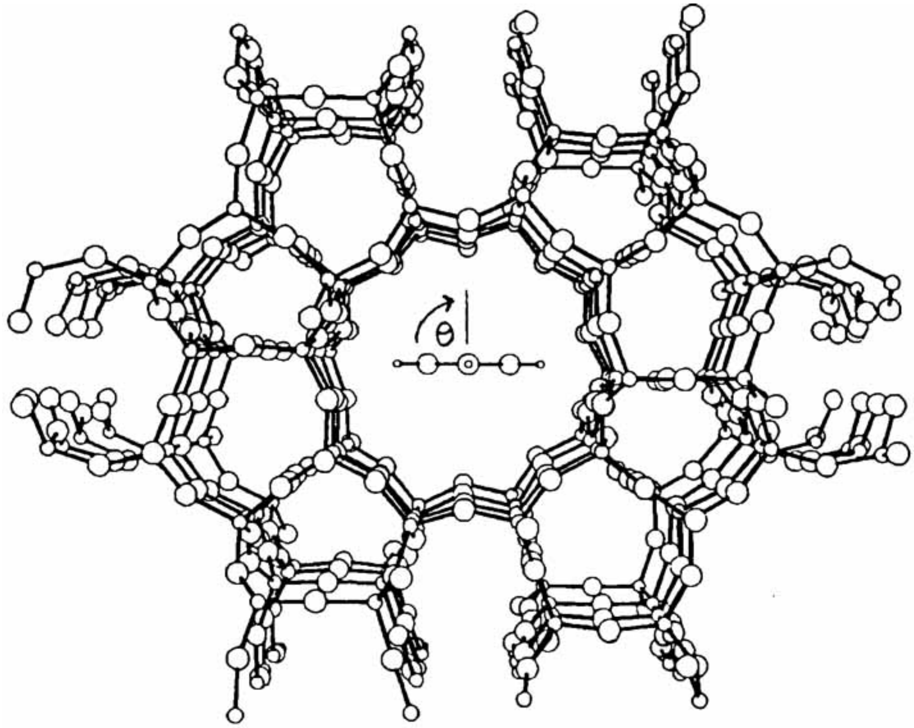

Figure 2 Straight channel projection of benzene in silicalite in its initial configuration. The unit cell length of this channel is 20 Å, and at 10 Å intervals this is intersected by sinusoidal channels running horizontally.

$$\Phi_{i,j} = \frac{A}{r^{12}} - \frac{B}{r^{6}} \qquad (1)$$

where r is the distance between two atoms i and j, and A and B are the repulsion and dispersion attraction constants. Following Kiselev *et al.* [5] we obtain the values of these constants from the reported polarizabilities of the O, C(sp^2), C(sp^3) and H atoms as given in Table 1. The pairwise interactions calculated from Equation (1) are then summed to give the total interaction energy of the molecule in the given position:

$$\Phi(tot) = \sum_{i,j} \Phi_{i,j} \qquad (2)$$

Table 1 Inter-atomic potential parameters for the interaction of hydrocarbon atoms with the zeolite framework.

	A ($kJ\,Å^{12}/mol$)	B ($kJ\,Å^{6}/mol$)
C(sp^2)—O	$1.44500 * 10^6$	$2.158 * 10^3$
C(sp^3)—O	$1.13873 * 10^6$	$1.701 * 10^3$
H—O	$1.49978 * 10^5$	$0.536 * 10^3$

The following approximations are used in the simulations attempted here:

1. The geometry of the frameworks is described by the reported crystal structures of these materials, and our calculations do not attempt to include any displacements or relaxations of atoms in the presence of the adsorbate molecule.
2. The potential energy is comprised entirely of the interactions between the adsorbate and the oxygen atoms defining the channels of the zeolite. Thus, interactions due to silicon atoms are ignored in the calculation.
3. The frameworks of theta-1 and silicalite are assumed to be free of aluminium. Since the starting materials used in the related experimental studies have high Si:Al ratios, it is appropriate to retain this assumption, which also allows us to neglect electrostatic terms in Equation (1).
4. The adsorbate molecules are assumed to be rigid in their equilibrium geometries.
5. No interactions between the adsorbate molecules have been included; this implies that the calculations are aimed at low loading of adsorbates.

In spite of the relative simplicity of the model used for the simulations, most of the approximations are particularly appropriate for the two zeolites examined here. Earlier calculations employing similar models have shown good qualitative and quantitative agreement with experimental observations [6–8].

In the adsorption of molecules at ambient temperature, molecules will not remain exclusively at the minimum energy site. The change in internal energy of the system on adsorption, and from this the enthalpy of adsorption, are obtained by integration over a large range of positions of the molecule in the zeolite framework. A Boltzmann factor accounts for the higher probability of occupancy of energetically more favourable sites. A rise in temperature increases the probability of occupancy of slightly less favourable sites, and we expect a decrease in the enthalpy of adsorption. The exact treatment used is described below.

COMPUTER SIMULATIONS

The series of calculations were set up from within the molecular graphics and modelling package "CHEMX" [9]. This allows one to take the crystallographic data on the zeolite structures and calculate all framework atoms within the boundaries of several unit cells. From the graphical representations of the framework one is able to retain a portion containing all oxygen atoms within a radius of 7 Å from the centre of the straight channel. The simulation is carried out over a 20 Å range along the channel. A benzene or toluene molecule is graphically manipulated to reside within the channel in a specified starting configuration (Figures 1 and 2). The molecule is then allowed to translate along and rotate about the molecular axis that is parallel to the channel axis. The interaction energies are then estimated and plotted as contour maps, in order to identify whether diffusion can occur readily or involves substantial energy barriers. They are also useful for finding the preferred molecular orientation for motion along the zeolite channels.

The internal heat of adsorption is defined as a ratio of two configuration integrals I_1 and I_2, taken over all volume available for adsorption:

$$\Delta U_{ads} = I_2/I_1 \tag{3}$$

where I_1 and I_2 are:

$$I_1 = \int \exp^{(-\Phi(tot)/RT)} \mathrm{d}v \qquad (4)$$

$$I_2 = \int \Phi(tot) \exp^{(-\Phi(tot)/RT)} \mathrm{d}v \qquad (5)$$

$\Phi(tot)$ is the total interaction energy calculated from Equations (1) and (2) above. The heat of adsorption is calculated as:

$$\Delta H_{ads} = \Delta U_{ads} - RT \qquad (6)$$

In this work, internal energies of adsorption were calculated for the benzene/theta-1 and the benzene/silicalite systems. In both cases interaction energies were estimated for the movement of the molecule along the channel direction, up/down and sideways movements, and rotation around the channel direction. These calculations were performed over one unit cell along the channel direction (approximately 10 Å for theta-1 and 20 Å for silicalite). This required the calculations of $\Phi(tot)$ at 9000 and 18 000 points, respectively.

In the diffusion simulation we allowed only two degrees of freedom for the molecule in the framework, a shift along the channel direction and a rotation around the axis describing the same direction. We use a relatively simplistic approach, in that we assume that the centre of the molecule remains in the centre of the channel. This was shown to be a better approximation for silicalite than for theta-1 by plotting the variation of interaction energies of benzene as the molecule shifts across the channel. Figure 3a shows the energy profile for the lateral shift of benzene in the straight channel of silicalite, and this confirms that the molecule is most likely to be situated in the channel centre. In theta-1, Figure 3b, we see that a shift of about 0.4 Å produces an interaction energy that is approximately 0.8 kJ/mol lower than that in the centre of the channel. Further movement of the molecule results in repulsion by the framework.

The colour coding for the contour maps (Figures 4 and 5) was chosen so that the darkest shade of blue represents the range of lowest, i.e. most favourable, interaction energies. The x-axis represents the distance between the centre of the molecule and a

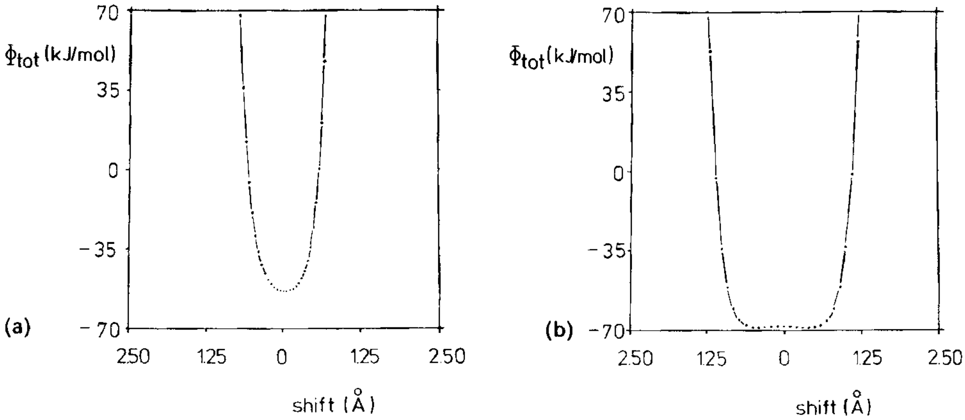

Figure 3 (a) Energy profile for the lateral shift of benzene in the straight channel of silicalite. (b) Energy profiles for the lateral shift of benzene in the channel of theta-1.

Table 2 Calculated internal energies of adsorption for benzene (toluene) at infinite dilution in theta-1 and silicalite.

T(K)	*Theta-1* $-\Delta U_{ads}$ *(kJ/mol)*		*Silicalite* $-\Delta U_{ads}$ *(kJ/mol)*	
198	67.8	(80.1)	55.5	(66.2)
298	66.9	(79.3)	54.8[a]	(65.5)
398	66.2	(78.6)	54.3	(65.1)
498	65.5	(77.9)	53.9	(64.7)

[a] Experimental value is -55 kJ/mol + RT ≈ -53 kJ/mol at 300 K[10].

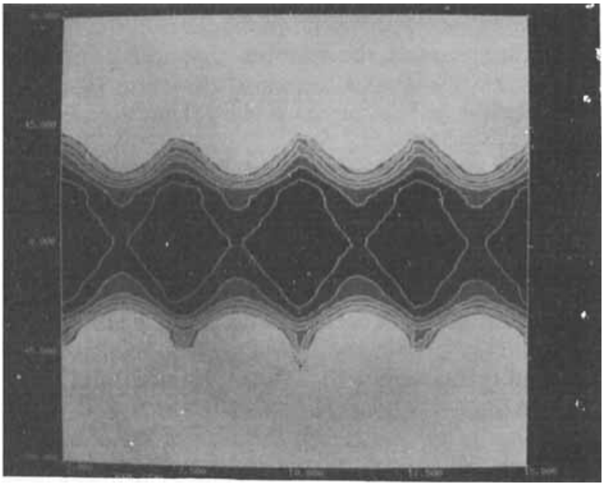

Figure 4a Energy contour map for the "parallel" diffusion of benzene in theta-1 (energy base level at −69 kJ/mol). (See colour plate V.)

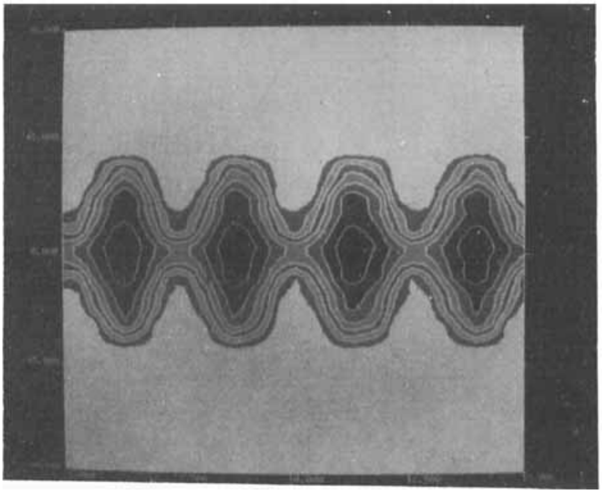

Figure 4b Energy contour map for the "perpendicular" diffusion of benzene in theta-1 (base level at −64 kJ/mol). (See colour plate VI.)

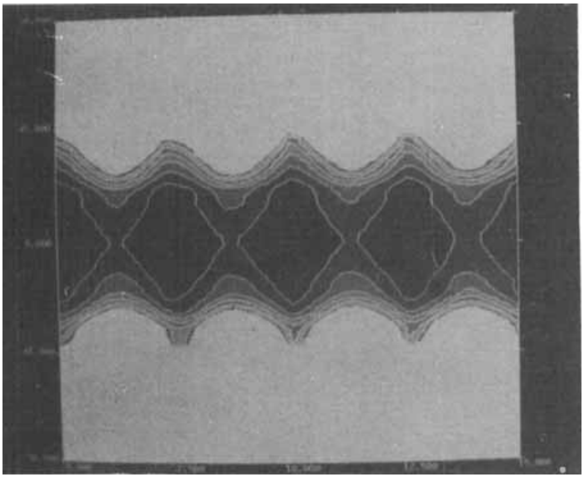

Figure 4c Energy contour map for the "parallel" diffusion of toluene in theta-1 (base level at −82 kJ/mol). (See colour plate VII.)

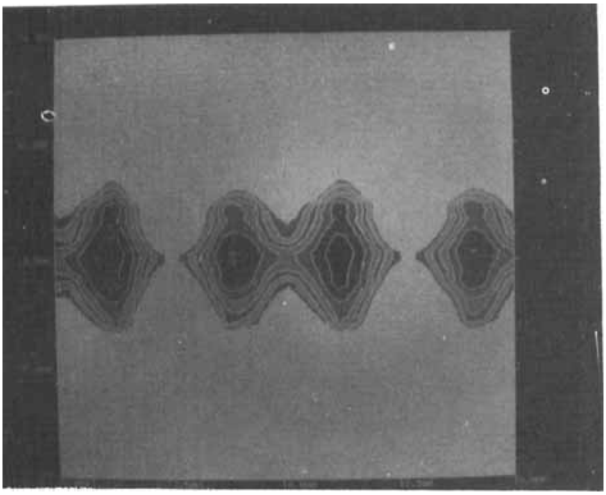

Figure 4d Energy contour map for the "perpendicular" diffusion of toluene in theta-1 (base level at −55 kJ/mol). (See colour plate VIII.)

notional reference atom, placed at 5 Å from the molecule along the channel direction at the start of the calculation. The y-axis indicates the amount of rotation (in degrees) of the molecule around the channel direction from the starting position (0°).

RESULTS AND DISCUSSION

The calculated values for the internal energies of adsorption at low loading of benzene and toluene in the two zeolites are shown in Table 2. The small decrease of $-\Delta U$ with temperature is due to the increased mobility of the adsorbate molecules and therefore the increased probability of occupying less favourable energy configurations. The

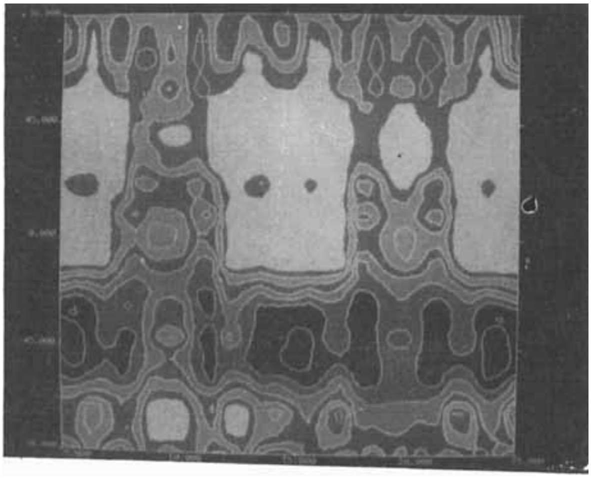

Figure 5a "Parallel" diffusion of benzene in silicalite (base level at −50 kJ/mol). (See colour plate IX.)

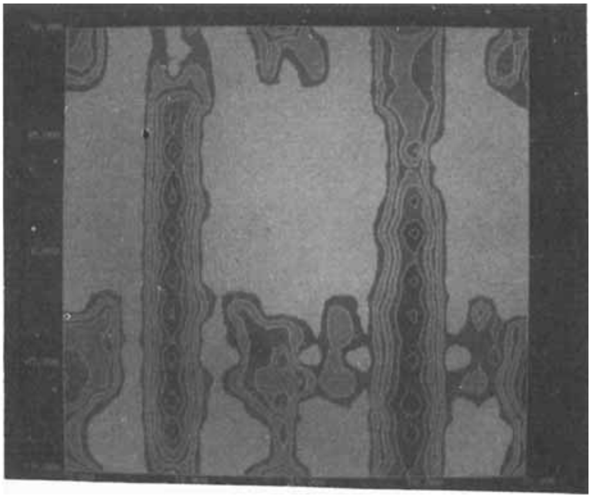

Figure 5b "Perpendicular" diffusion of benzene in silicalite (base level at −58 kJ/mol). (See colour plate X.)

calculated value ($\Delta H = -57.3$ kJ/mol) at 298 K is in good agreement with the experimental value (−55 kJ/mol) determined by Stach *et al.* [10]. A similar comparison cannot be made for the theta-1 system, since no experimental data were available. The lower energy of adsorption for theta-1 can be attributed to the closer fit of the adsorbate along the entire length of the channel.

Figure 4a shows the energy contour for benzene in theta-1, where the longest axis of benzene was assumed to lie parallel to the channel direction. The dark blue area shows that interaction energies remain within the lowest energy contour, provided the molecule does not rotate beyond ± 10 degrees from the starting configuration, and we can assume that the energy of activation lies between 0 and 22 kJ/mol. This rotational freedom increases at intervals of 2.5 Å to about 25°, indicating the passage through a constriction. When the calculations are carried out with the molecular axis of

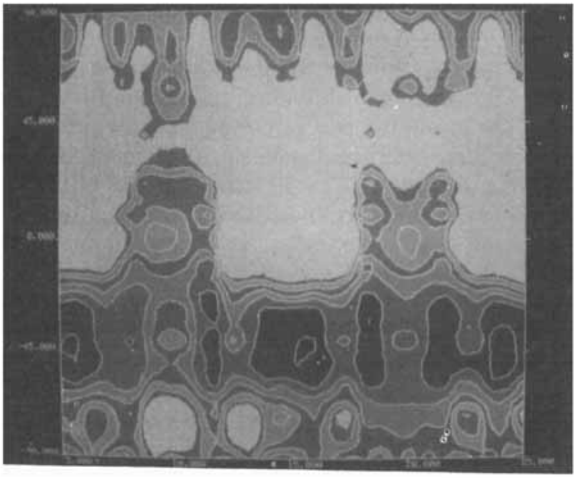

Figure 5c "Parallel" diffusion of toluene in silicalite (base level at −60 kJ/mol). (See colour plate XI.)

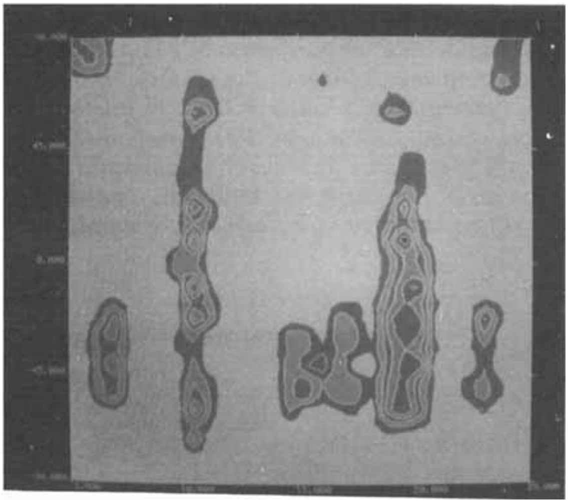

Figure 5d "Perpendicular" diffusion of toluene in silicalite (base level at −69 kJ/mol). (See colour plate XII.)

benzene lying perpendicular to the channel axis, we find an energy barrier of between 21 and 42 kJ/mol and also greater restrictions on molecular rotation (Figure 4b). We conclude that the latter will be highly strained and such a molecular diffusion is unlikely to occur.

Our calculations on toluene adsorption in theta-1, with the long molecular axis parallel to channel axis (Figure 4c), produced results similar to those for benzene; the difference in the magnitudes of the energies simply reflect the increased number of atoms in the adsorbate. The high energy barriers encountered for the "perpendicular" movements are shown in Figure 4d.

The energy contours for the diffusion of benzene and toluene in silicalite are shown in Figures 5a–5d. One of the striking features of these contours compared to those for theta-1 is the greater orientational freedom reflected in the low energy spread at the intersections at 10 Å and 20 Å along the channel. The small differences in the graphic details at these symmetry-related intersections are attributable to sampling artifacts, termination errors and the two different relative orientations of the sinusoidal channels with respect to the molecular diffusion paths considered here. The results, however, indicate that the minimum energy configurations along the straight channel are centred around molecular orientations 45 ± 10° from the starting configuration. We predict an activation energy of 22–45 kJ/mol for the diffusion of benzene and toluene in silicalite. This value could be increased by the reorientation of the molecule in the channel intersection from a "parallel" to a "perpendicular" orientation. The "parallel" movement for both benzene and toluene seems to have similar energy constraints; these results are also comparable to the energy contours obtained for silicalite with different Lennard-Jones parameters [11]. The "perpendicular" movement, however, involves higher energy barriers for toluene compared to benzene, as observed in theta-1.

In trying to probe whether there is an effective molecular traffic control for diffusion of adsorbates exclusively along the straight channels, we calculated interaction energies of benzene in the sinusoidal channels. The movement, which obviously requires a wobble and nutation along the long molecular axis, is as unrestricted as in the straight channel, but involves an energy barrier of approximately 25 kJ/mol on entering and leaving the channel at the intersections.

Recent sorption [12] and deuterium solid-state NMR studies [13] of hydrocarbons in silicalite and ZSM-5 complement some of the findings of these simulations. If the ratio of conversion of isomers over zeolites is directly related to the ability of the isomers to diffuse, then we can assume that the formation of *p*-xylene, with similar diffusion properties to toluene shown in Figures 4c and 5c, is preferential in theta-1, where the diffusion pathway is clearly less hindered. The diffusion of the *o*- and *m*-isomers, however, will be hindered in both zeolite systems.

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