

Diffusion of Cyclohexane and Alkylcyclohexanes in Silicalite

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The diffusion of cyclohexane and several alkylcyclohexanes in silicalite was studied using a simultaneous thermal analyzer. This apparatus allowed for the determination of heats of sorption and diffusion coefficients. Zero length chromatography was also used to determine diffusivities of some of the adsorbates. The trend in diffusion rates observed was *trans*-1,4-dimethylcyclohexane \gg methylcyclohexane $>$ cyclohexane $>$ ethylcyclohexane, *cis*-1,4-dimethylcyclohexane. This is in qualitative agreement with the previous results of Chon and Park. A comprehensive interpretation of the experimental results was developed, using the basic qualitative arguments of transition state theory. The fast diffusion of *trans*-1,4-dimethylcyclohexane is associated with a relatively low energy barrier for channel crossing. The transition entropy for diffusion appears to be the reason for the more rapid diffusion of methylcyclohexane relative to cyclohexane.

Introduction

Diffusion in zeolites has been the object of intense study and discussion for some decades. Many adsorbate/zeolite systems exhibit phenomena that do not appear in traditional Fickian diffusion processes. Weisz designated this diffusional regime as “configurational”.¹ Though ambiguous and restrictive, the definition is justified in that it recognizes the unique character of these transport processes.

The diffusion of cyclohexane in silicalite is a particularly interesting case, considering the large dimensions of the molecule (~ 5.8 Å) in relation to the zeolite’s pores (~ 5.5 Å). The initial studies of Chon and Park² on this system revealed some interesting results. Methylcyclohexane diffused somewhat more rapidly than cyclohexane and higher alkylcyclohexanes. Even more puzzling, *trans*-1,4-dimethylcyclohexane had a diffusion coefficient 2 orders of magnitude greater than any of the other molecules studied. The existence of a “window effect”³ was suggested as an explanation for the higher diffusivity of methylcyclohexane. However, it has been shown recently that the original phenomena on which the concept of “window effect” was based may not be real.^{4,5} No solid interpretation for the results with *trans*-1,4-dimethylcyclohexane was presented.

The objective of this work was to reexamine this system, to obtain further insight into the observed phenomena. A simultaneous thermal analyzer (STA) was employed, allowing for the measurement of heats of adsorption in addition to the rate of adsorption. A comprehensive interpretation of the results was attempted, on the basis of qualitative concepts of transition state theory.

Theory

In this work, most diffusivities have been determined gravimetrically. For diffusion in a parallel-side slab, the fractional mass uptake is described by Crank:⁶

$$\frac{m - m_0}{m_\infty - m_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{h^2}\right) \quad (1)$$

where h is the slab’s thickness and D the diffusion coefficient. At short times, eq 1 can be replaced by a simpler expression:

$$\frac{m - m_0}{m_\infty - m_0} = 4 \left(\frac{D t}{\pi h^2} \right)^{0.5} \quad (2)$$

According to eq 2, D can be computed from the slope of the initial linear portion of a plot of fractional uptake versus square root of time. This is the method most commonly employed in estimating diffusivities from gravimetric measurements. However, Balik⁷ has recently proposed a variation with some interesting advantages. Another asymptotic representation of eq 1, valid at long times, can be obtained by considering only the first term in the series:

$$\frac{m - m_0}{m_\infty - m_0} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 D t}{h^2}\right) \quad (3)$$

Equation 1 can then be approximated by a weighted average of the two asymptotic expressions (eqs 2 and 3):

$$\frac{m - m_0}{m_\infty - m_0} \approx \phi(x) f_{st}(x) + [1 - \phi(x)] f_{lt}(x) \quad (4)$$

where $x = Dt/h^2$, $f_{st}(x)$ and $f_{lt}(x)$ are given by eqs 2 and 3, respectively, and $\phi(x)$ is a continuous step function:

$$\phi(x) = \frac{1}{1 + \exp\left(\frac{x-a}{b}\right)} \quad (5)$$

$\phi(x)$ changes from 1 to 0 very rapidly in the neighborhood of $x = a$, making it the ideal weighing function for eq 4. The parameters a and b are chosen such that the error of the difference between eqs 1 and 4 is minimized. Values of $a = 0.053\ 26$ and $b = 0.001$ were shown to yield optimum results. The best value for a will depend on the particular geometry of the adsorbent particle. Equation 4 is a relatively simple analytical expression that can be used for numerically fitting the experimental uptake data to the theoretical model. Balik has proved the success of this technique (called the *hybrid one-term method*)

in the analysis of diffusion of small molecules in polymer thin films. One advantage lies in the fact that all the data are used in the fit, and good results may be obtained even when the data set has large scatter. In the traditional method, the linear portion of the uptake versus $t^{0.5}$ plot can be very small and difficult to identify. In addition, m_{∞} can be included as a fitting parameter in the hybrid one-term method, and therefore exact knowledge of the final loading is unnecessary. Finally, a graphical representation of eq 4 is practically indistinguishable from the complete solution (eq 1). This significantly simplifies the final comparison of the data to the model fit.

The other experimental technique used in this study was zero length chromatography (ZLC). This was developed in the late 1980s by Eic and Ruthven.⁸ It has been successfully applied to various zeolite/adsorbate systems^{9–12} and is now considered a reliable method for measurement of diffusivities. The carrier gas, containing initially a low constant concentration of adsorbate, flows through a small sample bed of adsorbent (only a few milligrams are used). After adsorption equilibrium is attained, the feed is switched to pure carrier gas. An FID detector monitors the concentration of adsorbate in the outlet stream, as it is desorbed from the sample. A mathematical model for the measured concentration as a function of time can be derived for a parallel-sided slab of thickness h :¹³

$$\frac{C}{C_0} = \frac{L}{2} \sum_{n=1}^{\infty} \frac{e - (\beta_n^2 Dt)}{\beta_n^2 + L(L+1)} \quad (6)$$

where the parameter L is defined as

$$L = \frac{1}{4} \frac{F \rho_s h^2}{m_s KD} \quad (7)$$

and β_n is given by the roots of

$$\beta_n \tan(\beta_n) = L \quad (8)$$

At long times, only the first term of the series remains significant, and eq 6 can be simplified to

$$\ln\left(\frac{C}{C_0}\right) = \ln\left(\frac{2L}{\beta_1^2 + L(L+1)}\right) - 4 \frac{\beta_1^2 Dt}{h^2} \quad (9)$$

The values of D and L can therefore be computed from the slope and intercept of a plot of $\ln(C/C_0)$ versus time.

Because of the small amount of sample employed, and the fact that the carrier gas flows directly through the sample, the ZLC method minimizes extracrystalline mass- and heat-transfer resistances, which may affect conventional gravimetric measurements, especially for rapidly diffusing systems.

Experimental Section

The silicalite used in these study was synthesized at W. R. Grace with a nominal Si/Al ratio greater than 500/1. The crystals have the typical coffin-shape form and a relatively narrow size distribution. The dimensions are (thickness \times width \times length) $8.9 \times 9.4 \times 39.0 \mu\text{m}$.

The zeolite was calcined at 450°C for 12 h under air flow. Before use, each sample was activated in the experimental apparatus at 500°C for 12 h under dry helium flow. Heating ramps were never above $10^\circ\text{C}/\text{min}$.

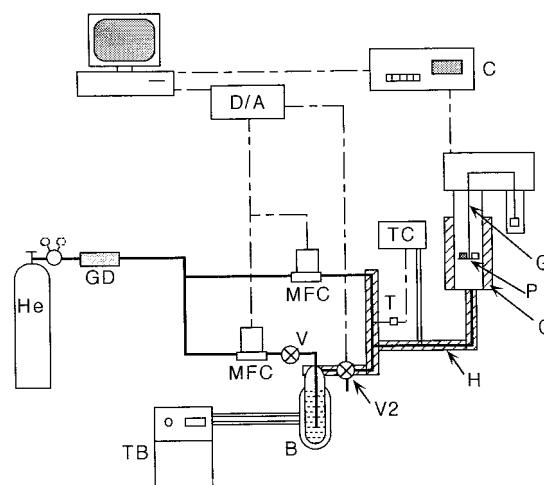


Figure 1. Setup of STA apparatus. B = bubler with adsorbate; C = STA's control unit; G = TGA hagdown assembly; GD = gas drier; H = heating tape; MFC = mass flow controller; O = STA's oven; P = DSC heat flux plate with sample and reference pans; T = thermocouple; TB = thermostatic bath with circulation; TC = temperature controller for region H; V = valve; V2 = two-way valve.

All adsorbates were obtained from Aldrich Chemical Co. (purities $> 99\%$), except for *trans*-1,4-dimethylcyclohexane, which was obtained from Fluka Chemika (purity $> 98\%$).

Most of the experimental work was performed with a simultaneous thermal analyzer (Rheometrics STA 625). A schematic of the experimental setup is shown in Figure 1. This apparatus combines a microgravimetric balance (TGA) with $0.5\text{-}\mu\text{g}$ maximum resolution and a differential scanning calorimeter (DSC) with $5\text{-}\mu\text{W}$ maximum sensitivity. Gravimetric and calorimetric data can be collected simultaneously from a single sample. Approximately 10 mg of zeolite were used in each experiment, spread as thinly as possible in the sample pan (about 1 cm in diameter). The runs were conducted under high-purity helium flow ($40\text{--}60 \text{ cm}^3 \text{ min}^{-1}$, typically). The adsorbate was introduced in the gas stream via a bubbler. The concentration in the gas phase could be varied by changing the relative flow rates of the bubbler and diluent streams and the bubbler's temperature. The STA apparatus was interfaced with a personal computer for data acquisition and control, using native Rheometrics' hardware and software. The mass flow controllers and valve associated with the gas streams were also interfaced with the same computer, using a μMAC 4000 A/D board.

The ZLC experiments were based on a typical setup¹⁴ (see Figure 2). A Hewlett-Packard 5790A gas chromatograph equipped with a FID detector was employed. The sample (about 2 mg) was held in place by two stainless steel frits in a 1/8 in. Swagelok union. Tubing of 1/16 in. was always used if possible, to minimize dead time effects. The carrier gas was high-purity helium. All data acquisition and device control was again done with a personal computer, using a μMAC 1050 A/D board.

Results

STA Experiments. The STA apparatus collects gravimetric and calorimetric data simultaneously. Figure 3 shows a typical set of data for adsorption of methylcyclohexane in silicalite. The heats of sorption are given by the integral area of the heat flow curve, while the diffusion coefficients are estimated from the gravimetric uptake data. The hybrid one-term method described above was used in the computation of the diffusion coefficients. Some representative uptake curves are shown in

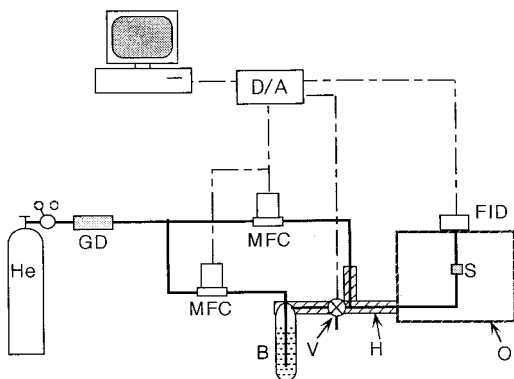


Figure 2. Setup of ZLC apparatus. B = bubbler with adsorbate; FID = flame ionization detector; GD = gas drier; H = heating tape; MFC = mass flow controller; O = GC's oven; S = sample; V = two-way valve.

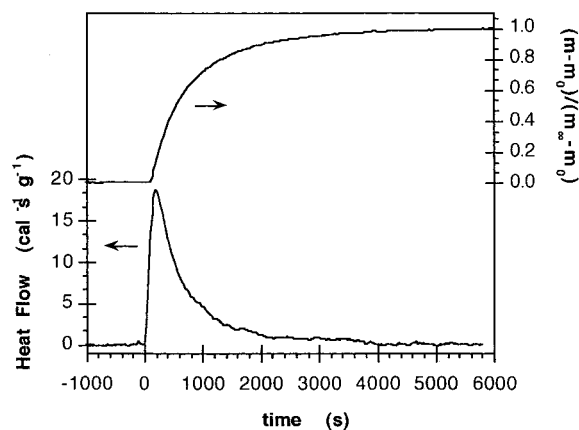


Figure 3. Gravimetric and calorimetric data obtained for methylcyclohexane adsorption at 150 °C.

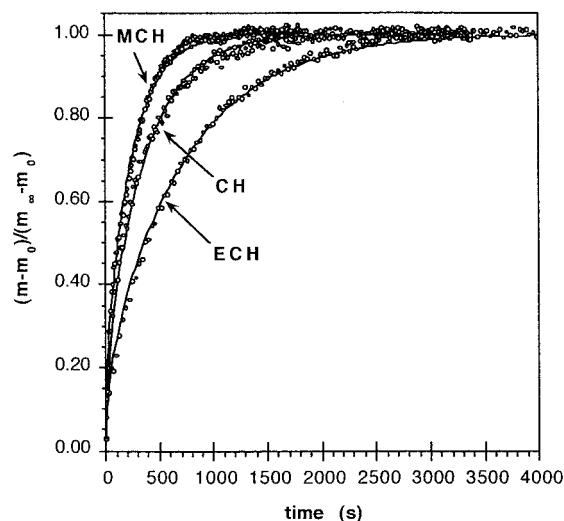


Figure 4. Typical gravimetric uptake curves for adsorption of cyclohexane (CH), methylcyclohexane (MCH), and ethylcyclohexane (ECH) at 200 °C. The solid lines are the fits of the diffusion model (eq 1).

Figure 4. It can be seen that the theoretical model gives a very good representation of the data over the entire time range of measurement. This, together with the fact that different sample amounts (between 10 and 20 mg) gave consistent results, indicates that no extraneous mass- or heat-transfer effects affected the measurements.

A maximum loading capacity of about 4 molecules per unit cell was observed for all adsorbates. To detect a possible

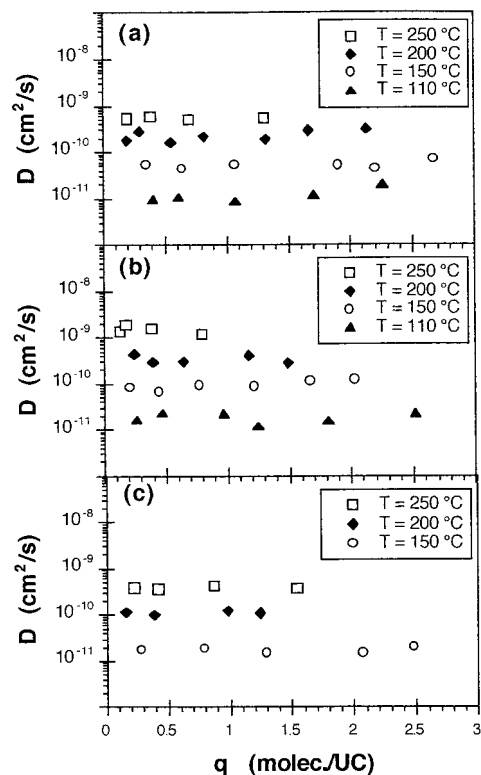


Figure 5. Diffusivities as a function of loading for (a) cyclohexane, (b) methylcyclohexane, and (c) ethylcyclohexane.

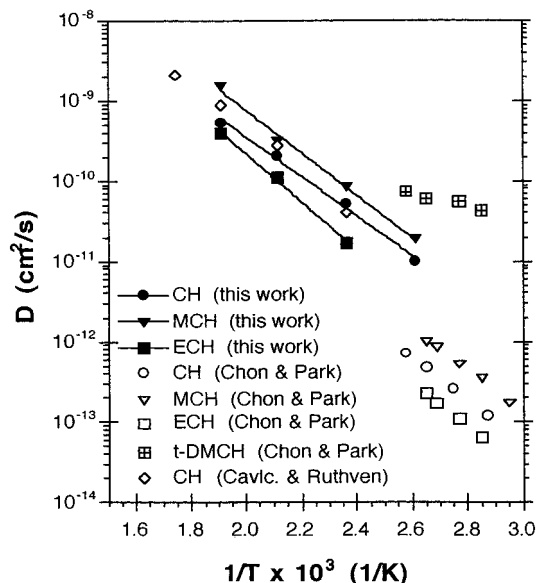


Figure 6. Arrhenius plots of diffusivities measured gravimetrically. Results of Chon and Park [1988] and Cavalcante and Ruthven [1995] are also shown.

dependence of the diffusivity on concentration, small sorption steps were performed at different zeolite loadings. There was good agreement between desorption and adsorption curves. The computed diffusivities for cyclohexane (CH), methylcyclohexane (MCH), and ethylcyclohexane (ECH) are shown in Figure 5. These diffusivities appear to be independent of loading. This is consistent with the results of Cavalcante and Ruthven¹⁵ for diffusion of cyclohexane in silicalite.

In Figure 6, the average diffusivities for each temperature are plotted versus $1/T$. The data are well-represented by an Eyring-type expression ($D = A \exp(-E_a/RT)$). The values obtained for CH in this work are quite close to the results of

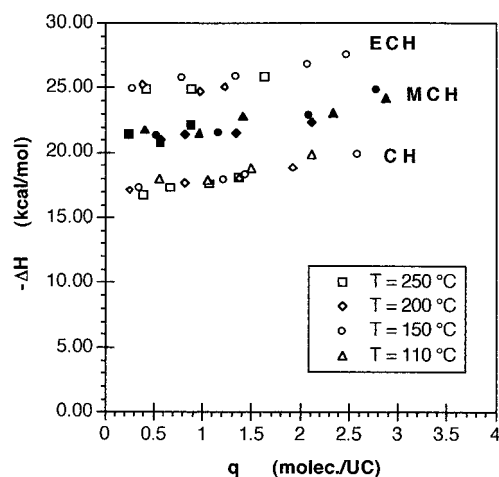


Figure 7. Heats of sorption as a function of loading.

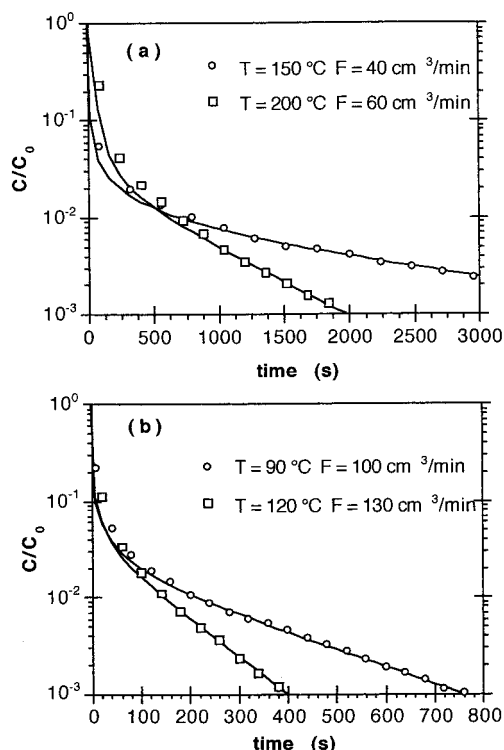


Figure 8. Typical experimental ZLC curves for cyclohexane (CH) and *trans*-1,4-dimethylcyclohexane (*t*-DMCH).

Cavalcante and Ruthven.¹⁵ The data of Chon and Park² are also plotted in Figure 6. Our results show the same relative trend in the diffusivities of the three adsorbates (MCH > CH > ECH), but the values are about 1 order of magnitude larger. It is important to note that those authors used very small crystals in the experiments (less than 1 μm thick). Under these conditions, extraneous effects may become significant. This fact was also discussed by Cavalcante and Ruthven,¹⁵ who indeed observed a difference of about 1 order of magnitude in the measured diffusivities of CH with sets of large and small crystals.

The heats of adsorption measured for CH, MCH, and ECH at different loadings are shown in Figure 7. Adsorption and desorption measurements gave consistent results. A slight increase in the heats of adsorption with loading is apparent. This may be attributed to increasing adsorbate–adsorbate interactions. The isosteric heats measured by Cavalcante and Ruthven¹⁵ for CH show a similar trend, but were about 10% lower.

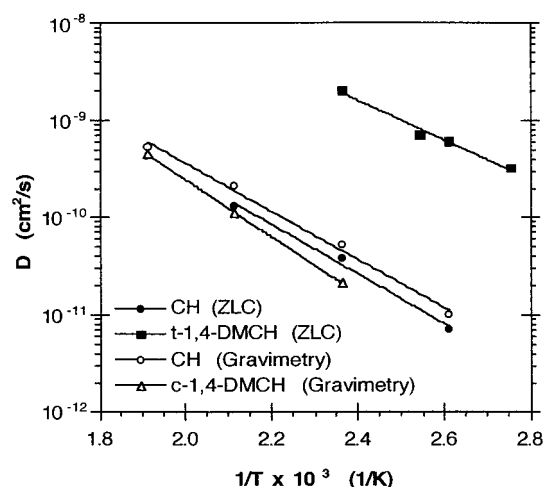


Figure 9. Arrhenius plots of diffusivities measured with the ZLC technique for cyclohexane (CH) and *trans*-1,4-dimethylcyclohexane (*t*-DMCH). Gravimetric measurements for CH and *cis*-1,4-dimethylcyclohexane (*c*-DMCH) are also shown.

TABLE 1: Activation Energies for Diffusion of Cyclohexane and Alkylcyclohexanes in Silicalite

	E_a (kcal/mol)		
	this work	Chon and Park [1988]	Cavalcante and Ruthven [1995]
cyclohexane	11.5	12.1	12.8
methylcyclohexane	12.2	11.7	
ethylcyclohexane	13.8	12.9	
<i>n</i> -propylcyclohexane		13.2	
<i>n</i> -butylcyclohexane		15.8	
<i>n</i> -pentylcyclohexane		20.0	
<i>trans</i> -1,4-dimethylcyclohexane	9.3	5.7	
<i>cis</i> -1,4-dimethylcyclohexane	13.4		

ZLC Experiments. We observed that *trans*-1,4-dimethylcyclohexane (*t*-DMCH) indeed diffuses significantly faster than the other adsorbates studied. The time scale of the gravimetric measurements being much shorter, intrusion of extracrystalline resistances is possible, and the method cannot be used with confidence. We therefore used ZLC in the measurements for *t*-DMCH. The nature of this technique minimizes these extraneous effects. To test the consistency of the two methods, ZLC measurements for CH were also performed.

Representative experimental data are shown in Figure 8, for both CH and *t*-DMCH. The theoretical diffusion model, also plotted, describes the data well. The values computed for the parameter L were always sufficiently large ($L > 50$) to guarantee that the process was not equilibrium-controlled.¹¹ The Arrhenius plot of the measured diffusivities is shown in Figure 9. There is reasonable agreement between the CH diffusivities measured with the two techniques. The diffusivities measured for *t*-1,4-DMCH are more than 1 order of magnitude larger than for CH. Also shown in Figure 9 are the results for *cis*-1,4-dimethylcyclohexane (*c*-DMCH), measured gravimetrically.

The activation energies computed from the Arrhenius plots for all adsorbates are shown in Table 1. The activation energy obtained for CH in this work agrees well with those from the prior studies. We observe an increasing trend in E_a with the length of the alkyl group, similar to the results of Chon and Park.² There is however significant discrepancy for *t*-DMCH. One must again note that these authors used smaller crystals, and their measurements may have been masked by extracrystalline mass- or heat-transfer resistances. This would be

particularly pertinent for a relatively fast diffusing adsorbate such as *t*-DMCH.

Discussion

The following trend in the diffusion rates was observed in this work: *t*-DMCH \gg MCH > CH > ECH, *c*-DMCH. Two main questions arise: why does *t*-DMCH have a much greater diffusivity than any of the other molecules, and why does MCH diffuse somewhat faster than CH? We develop below a general reasoning that will allow for a satisfactory interpretation of these results.

The framework of silicalite is composed of two intersecting channel systems: straight channels (slightly elliptical, diameters 5.1 and 5.7 Å) and zigzag channels (nearly circular, 5.4 Å diameter). The channel intersections form a spherical "cavity" with a diameter of about 8.7 Å.¹⁶ The straight channels are oriented perpendicularly to the crystal's larger surface (i.e., along the crystal thickness direction). We believe that diffusion of cyclohexane and alkylcyclohexanes occurs principally along these channels. This assumption is supported by the fact that, in our work and in prior work,^{2,15} the one-dimensional diffusion model for a parallel-sided slab affords the best fit of the experimental sorption curves. If diffusion along the zigzag channels were significant, a cylindrical or spherical diffusion model would probably give the best results. A similar analysis, performed in detail by Ruthven and co-workers,⁹ indicated that also aromatic adsorbates diffuse preferentially along the straight channels of silicalite. Müller and Conner¹⁷ used in situ X-ray diffraction and FTIR during adsorption of cyclohexane and also conclude that CH does not access the zigzag channels.

Diffusion in zeolites may be viewed as an activated process. Transport along the zeolite framework involves activated "jumps" of the diffusing molecule between adjacent equilibrium adsorption sites. The size of the cyclohexane molecule can be characterized in terms of a kinetic diameter of 6.0 Å¹⁸ or 5.7 Å (from the Wilke and Lee method¹⁹). However, the methylcyclohexanes are even larger, to greater than 9 Å for the ethyl- or dimethylcyclohexanes. Considering the dimensions of the framework, it is clear that the equilibrium sites will correspond to the ring being positioned at channel intersections. This is in agreement with the measured maximum adsorption capacities of 4 molecules per unit cell, corresponding precisely to 1 molecule per intersection.^{2,17,15} The same is valid for the alkylcyclohexanes. The alkyl group will be accommodated so that interactions with the framework are maximized. Due to the small cross-sectional diameter of the alkyl group, it may be at least partially inserted (adsorbed) in the channel while the cyclohexane ring lies in the intersection. The transitional jumps will involve passage of the molecules through the channels, where it will suffer strong repulsions from the walls, due to the ring's large dimensions.

This visualization of the diffusion process will be useful in the interpretation of the experimental results. Figure 10 shows the measured heats of adsorption ($-\Delta H$), diffusional activation energies (E_a), and calculated preexponential factors (A). The heat of adsorption reflects the interactions of the molecule with the framework at the equilibrium state. The increase in $-\Delta H$ in the sequence CH, MCH, ECH (Figure 10a) is certainly due to an increase in favorable interactions associated with the presence of the alkyl group. The longer and more flexible the alkyl, the higher is the adsorption strength. *t*-DMCH, however, shows a somewhat lower heat of adsorption than ECH, despite both molecules possessing the same number of carbon atoms. The ethyl group in ECH may be more strongly adsorbed (maybe

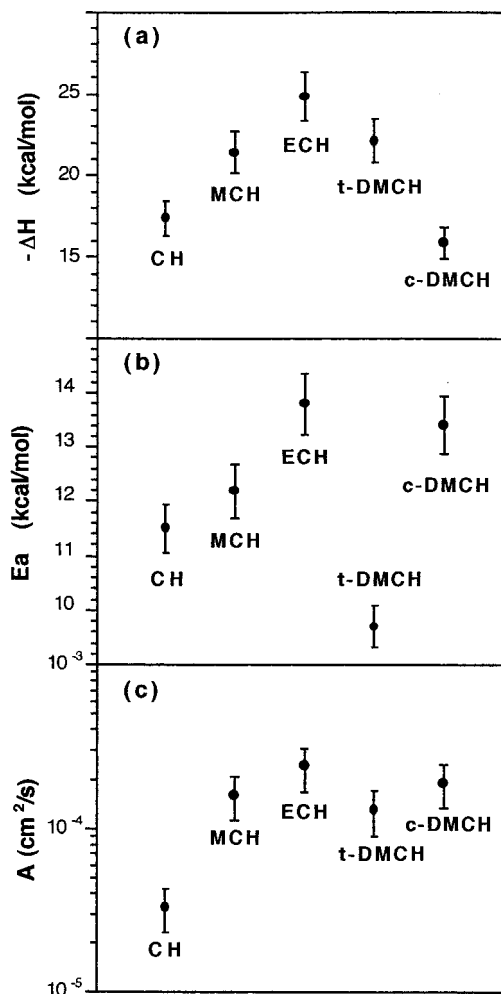


Figure 10. Computed values of heats of sorption ($-\Delta H$), activation energies (E_a), and preexponential factors (A) for all the adsorbates studied. Rough estimates of the errors are also shown.

adsorbed deeper into the channel) than the two methyl groups in opposite ends of the ring in *t*-DMCH. Interestingly, *c*-DMCH exhibits the lowest heat of adsorption. The position of the two methyl groups in the cis configuration impairs the molecule's interaction with the zeolite. Because of this steric effect, the ring of *t*-DMCH itself is less strongly adsorbed at the intersection.

The activation energy (Figure 10b) is associated with the height of the potential energy barrier involved in the passage through the transition state, between adjacent equilibrium sites. The magnitude of the barrier depends on the relative energy levels at the equilibrium and transition states. The increase of activation energy with the length of the alkyl group observed in this work (ECH > MCH > CH) (see also Chon and Park,² Table 1) can be related to the increase in adsorption strength. In the ground state (equilibrium), ECH is at a "deeper" potential energy level than CH. When the molecule passes through the channel, its energy level is essentially determined by the repulsions exerted on the ring, and the presence of the alkyl has little effect. Therefore, ECH has an higher energy barrier for diffusion. More puzzling is the fact that *t*-DMCH has the lowest activation energy of all the molecules studied, while the heat of adsorption for *t*-DMCH is close to that for MCH. Therefore, its lower E_a has to be attributed to a more favorable passage through the channels. Why can the trans configuration facilitate this process so significantly? Detailed simulations of molecular potentials would be able to provide further insight.

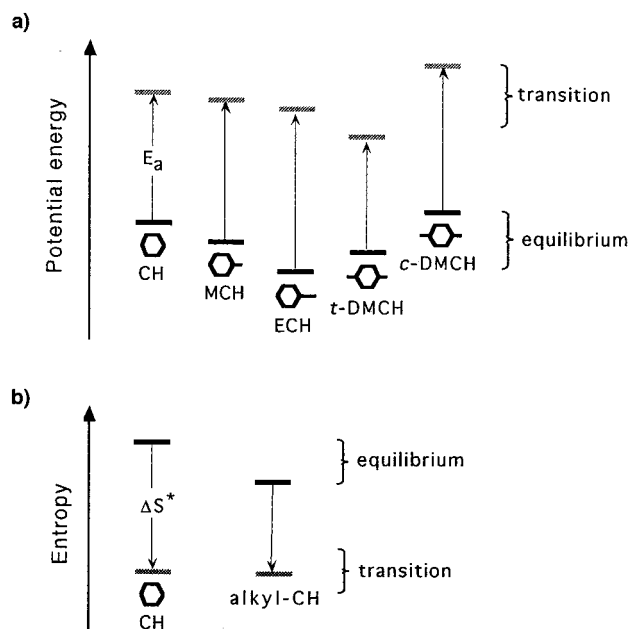


Figure 11. Schematic mapping of (a) potential energy and (b) entropy levels in the equilibrium and transition diffusional states.

On the other hand, the high value of E_a measured for *c*-DMCH may be interpreted in terms of a very difficult passage through the channels, due to the less favorable configuration.

One must also realize that the cyclohexane ring can be in either boat or chair conformations, and the chair conformer is certainly favored in the transition state because of its lower profile (cross section). Indeed, the chair conformation is favored in the gas phase by ~ 5 kcal/mol for cyclohexane and ~ 3.6 kcal/mol for the 1,4-*trans*-DMCH.²⁰ The methyl (or ethyl) groups will also tend to retain the molecules in the chair conformer, as they will lead (or follow) the molecule through the straight channels. Indeed, the C8 cycloalkanes are larger in longest dimension than the channel intersections. *trans*-Dimethylcyclohexane in particular is certainly constrained to the chair conformer with methyls aligned with the straight channel axis. *trans*-DMCH is, thus, directed, entering and exiting the channel intersections, and has limited ability to change conformation and/or to maximize interactions with the pore walls. Thus, both the entropy and the energy of interactions of *t*-DMCH at the channel intersections are decreased relative to the other cyclohexanes. This would result in a decrease in differences in the entropy and energy between *trans*-DMCH molecules at the channel intersections and the transition state (between the intersections). In terms of transition state theory this would mean an increasing preexponential factor (lower decrease in entropy between equilibrium and transition states) and a decreasing activation energy for diffusion (higher relative energy at the intersections).

The energy relationships are illustrated schematically in Figure 11a. The relative location of the energy level at equilibrium is given by the values of the heats of adsorption, and the length of the energy "jump" is proportional to the activation energy.

The higher diffusivity of MCH in relation to CH is not associated with a lower activation energy, but with a higher preexponential factor (A). It seems that, for the sequence CH, MCH, ECH, there is an increase in activation energy simultaneously with an increase of the preexponential factor (see Figure 10b,c). This suggests the existence of a *compensation effect*. According to this theory, a correlation between activation energy

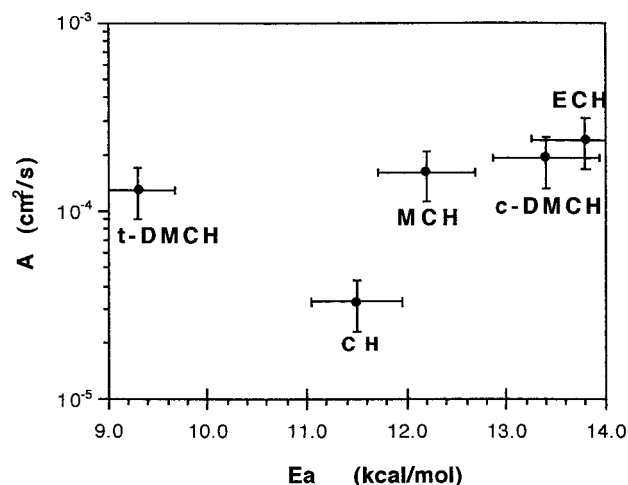


Figure 12. Preexponential factors (A) plotted versus activation energies (E_a) for all the adsorbates studied.

and transition entropy is expected, in related processes, because they are effectively interdependent. In other words, an increase of the activation energy may require an increase of the entropy of transition. Justifications of this effect, as well as references to its occurrence in many fields of study, have been analyzed by Conner et al.^{21,22} and in references presented therein. An "isokinetic" relationship is often observed experimentally, viz.,

$$\ln A = \ln b + aE_a \quad (10)$$

where a and b (related to the "isokinetic" temperature) are constants. A plot of the values of $\ln A$ versus E_a obtained in this work is shown in Figure 12. A linear relationship is not evident, and thus, compensation may exist but an isokinetic temperature is not evident. All the alkylcyclohexanes have relatively similar values for A , while cyclohexane falls outside this group, showing a lower preexponential factor. A compensation effect might be present, but the dominant influences may be those that affect the entropy of transition, common to the alkylcyclohexanes. This might be the constrained environment of the zeolite where the alkyl substituents restrict the transformation between boat and chair conformations at the channel intersections.

Qualitative arguments from transition state theory can provide an interpretation for this problem. The diffusion coefficient can be expressed following Eyring's theory of rate processes:²³

$$D = \lambda \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-E_a}{RT}\right) \quad (11)$$

The "preexponential" factor A is then a function of ΔS^* , the difference in molecular entropy between the transition and equilibrium states. This can be detailed in terms of the partition functions for the two states^{14,24,25} (low adsorbate concentration and negligible adsorbate-adsorbate interaction is assumed):

$$D_x = \frac{\lambda_x^2 kT}{2 h q_x q} \exp\left(\frac{-V_{0x}}{kT}\right) \quad \text{with} \quad \frac{q^*}{q} = \frac{q_v^* q_z^* q_{rot}^* q_{int}^*}{q_y q_z q_{rot} q_{int}} \quad (12)$$

The following partition functions have been introduced: translational (q_x, q_y, q_z), rotational (q_{rot}), and internal vibration (q_{int}). The superscript * designates the transition state. x is the direction of diffusion and V_{0x} the height of the energy barrier for passage, along x , to a neighboring site. When crossing the channel, a molecule will be significantly more restrained than

when it resides at the intersection. There is, therefore, a loss of translational and rotational degrees of freedom. The more significant the difference in entropy between the equilibrium and transition states, the lower will be the ratio q^*/q in eq 12, or the entropic term $\exp(\Delta S/R)$ in eq 11 (recall that $\Delta S^* < 0$). When considering cyclohexane and the alkylcyclohexanes, it seems reasonable to expect that CH will have the highest mobility in the equilibrium state. It is not clear whether cyclohexane is actually able to rotate in the intersection or to alternate between chair and boat conformations, but it will certainly have more degrees of freedom than the molecules with alkyl groups which may, as noted before, be partially adsorbed in the channel. On the other hand, the entropy in the transition state must be close for all molecules, since all should be similarly restricted when crossing the channel (the constriction of the ring being the determining factor). Consequently, CH must have the lowest preexponential factor, in agreement with the experimental results (Figure 10c). Figure 12b illustrates these considerations. This lower transition entropy is responsible for the higher diffusivity of MCH in relation to CH. For ECH, however, the increase in activation energy is overwhelming, causing the diffusivity to decrease.

The phenomena described above is a case of *intracrystalline partitioning*, as introduced by Xiao and Wei.¹⁶ In their study of diffusion of *n*-paraffins in zeolite 5A, they have shown quantitatively that differences in rotational degrees of freedom, induced by different molecular lengths, can have a very significant effect on the preexponential factors.

The high diffusivity of *t*-DMCH in relation to CH is due to the combined effects of lower activation energy and a favorable entropic effect (higher preexponential factor). It is important to note that an apparently similar phenomenon is exhibited with diffusion of *p*-xylene and benzene in silicalite. We note the recent work of Rees and co-workers,^{26,27} using a frequency response technique. The diffusion coefficient for *p*-xylene in the straight channels was 2 orders of magnitude greater than for benzene. The activation energy was 25% lower for *p*-xylene and the preexponential factor was about 1 order of magnitude higher. The parallel between the two systems is evident.

Conclusions

The trend in the diffusivities observed by Chon and Park was reproduced in this work. The measured heats of adsorption and activation energies allowed for a mapping of the potential energies of the adsorbates at the equilibrium and transition diffusional states. A better understanding of the observed relative diffusion rates can be obtained this way. *trans*-1,4-Dimethylcyclohexane seems to go through a relatively low energy barrier when crossing the channels, thus having a significantly lower activation energy than the other molecules. In addition to potential energy barriers, entropic factors also seem to play a significant role in this system. The alkylcyclohexanes are more restricted at the channel intersections than cyclohexane, which favors diffusion. This entropic effect may be responsible for the greater diffusivity of methylcyclohexane in relation to cyclohexane. The *trans* isomer of dimethylcyclohexane could be the most sterically restricted to the chair conformer. This would increase the preexponential factor for diffusion by decreasing the entropy and the ability of the molecule to maximize its interaction (heat of adsorption) in the channel intersections. The *cis* isomer of dimethylcyclohexane interacts too much within the pores and can only be adsorbed in a strained configuration (reducing the net enthalpy of adsorption) and, further, does not easily diffuse easily between

channel intersections, as it does not easily adopt the favorable chair configuration in this restricted environment. The ethyl cyclohexane is adsorbed more strongly due to the ability of the ethyl to interact with the zeolite pore walls.

Diffusion in zeolites (and other porous networks) is certainly dictated by two factors: (1) the difference in energies between equilibrium states and the transitions between them and (2) the difference between the constraints on the diffusing species in these two states. If the energy and entropy of transition states are similar, as we conclude they are in these studies, species may be more strongly adsorbed because of their ability to interact with the surface, and this potential for interaction may also reflect the ability of the molecule to change conformation. There would, thus, be a connection between the ability of a molecule to maximize its interaction with the surface (increasing the heat of adsorption at the equilibrium state) and an increased difference in entropy between the equilibrium and transition states. Since the entropy difference between equilibrium and transition states is negative, this would result in a compensation between the availability (activation energy) and accessibility (transition entropy) of diffusion in zeolites. This compensation is somewhat unconventional in that the dominant differences between these systems involve differences in the equilibrium states and not differences in the transition states.

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Glossary

A	preexponential factor (cm ² /s)
C	concentration of adsorbate in the gas phase (mol/cm ³)
C_0	initial concentration of adsorbate in the gas phase (mol/cm ³)
D	diffusion coefficient (cm ² /s)
ΔS^*	entropy difference between transition and equilibrium states
E_a	activation energy (kcal/mol)
F	carrier gas flow rate (cm ³ /s)
$\phi(x)$	weighing function defined by eq 5
$f_{lt}(x)$	long time asymptotic solution of eq 1
$f_{st}(x)$	short time asymptotic solution of eq 1
h	particle thickness (cm); Planck constant in eq 10
K	adsorption equilibrium constant (Henry's law constant)
k	Boltzmann constant
L	parameter defined by eq 7
λ_x	distance between two adjacent equilibrium sites
m	amount adsorbed (g)
m_0	initial mass adsorbed (g)
m_s	mass of zeolite sample (g)
m_∞	final mass adsorbed (g)
q	partition function at the equilibrium state
q^*	partition function at the transition state
R	ideal gas constant (cal mol ⁻¹ K ⁻¹)
ρ_s	density of zeolite sample (g/cm ³)
t	time (s)
T	temperature (K)
V_{0x}	height of the energy barrier for diffusion in the x direction
x	adimensional time, $=Dt/h^2$

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