**Diffusion in Zeolites**

# Accelerated Diffusion of Long-Chain Alkanes between Nanosized Cavities**

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Normally, the mobility of molecules decreases with increasing molecular weight. This is true in liquids and also in porous media, where the transport properties of the liquid have a major influence in various applications such as catalysis and separation. In nanoporous materials, the notion of liquid phase is not applicable, since each adsorbed molecule interacts with the solid. The molecules are geometrically constrained, either by their size or by their orientation. This is the basis of shape-selective catalysis with zeolites. For example, cracking of heavy alkanes in small-pore zeolites such as erionite gives unusual product distributions, with maxima at approximately $C_4$ and $C_{12}$ and a clear minimum at $C_8$.[1] This was one of the first examples of what has been termed "product molecular shape selectivity". Gorring studied experimentally the diffusion of several *n*-alkanes in zeolite T (an offretite/erionite intergrowth), in which the less open erionite cages act as bottlenecks for diffusion.[2] He found that molecules in the $C_{12}$ range diffused about two orders of magnitude faster than those in the $C_8$ range. He proposed that the product distribution in the cracking reaction was due to this anomalous transport phenomenon.[2] The term "window effect" was coined to designate the higher transmittance of the erionite cages for molecules of a given critical length.[2] However, since no other group could find such a periodic variation in diffusivity (e.g., ref. [3]), the existence of the window effect is one of the most controversial topics in zeolite science.

Zeolites are ideal models for microporous materials, because the dimensions of the cages and pores of these crystalline structures are known with accuracy. In NaX zeolite, the framework consists of cages connected by windows with a nominal diameter of 7.4 Å. For a homologous series of *n*-paraffins, a monotonous decrease in the diffusion coefficient with increasing molecular weight was found by pulsed-field gradient NMR (PFG NMR) spectroscopy (Figure 1a). A similar trend was found by quasielastic neutron scattering (QENS) in ZSM-5, the structure of which consists of intersecting channels with a free diameter of about 5.5 Å (Figure 1b). In NaCaA zeolite, the cavities are interconnected by windows with a nominal diameter of 4.1 Å, based on an radius of 1.35 Å for oxygen. The effective radius of oxygen is in fact close to 1 Å, so that the free diameter of the windows is not far from 5 Å, hence the product name zeolite 5A. Zeolite 5A is used in numerous adsorption processes because, like erionite, it adsorbs linear alkanes while rejecting branched ones. Due to the narrow pores, the diffusivities of *n*-alkanes in this structure are too low to be measured by conventional QENS instruments, but they are accessible by the neutron spin echo (NSE) technique.

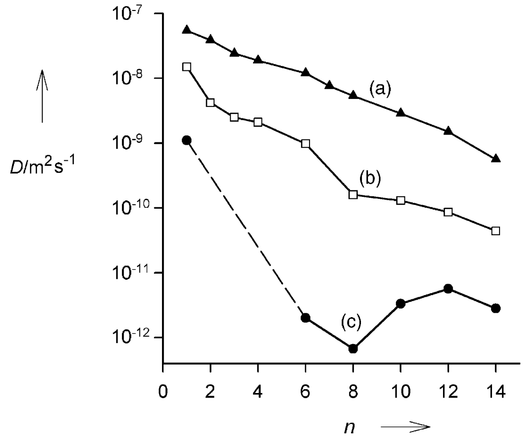

***Figure 1.*** Diffusion coefficients of linear alkanes in various zeolites, obtained by different techniques at 475 K, as a function of the mumber of carbon atoms. a) In NaX zeolite by PFG NMR spectroscopy,[9] b) in ZSM-5 by QENS,[10] and c) in zeolite 5A by NSE. Diffusivities for methane and *n*-hexane are taken from references [11] and [6], respectively. The values from the literature were extrapolated to 475 K by using the reported activation energies. The solid and dashed lines are only guides for the eye.

The NSE technique is unique in the sense that one can measure very small velocity changes for neutrons scattered from the sample (on the order of $10^{-5}$). The original idea is based on the determination of the Larmor precession angle of the neutron spin in a strong magnetic field of varying intensity.[4] Small energy changes lead to a decreased polarization, or amplitude, of the echo. The echos are measured for different field integrals, corresponding to varying Fourier times. A recently built NSE spectrometer at the Institut Laue-Langevin[5] is able to probe long times (hundreds of nanoseconds) and it allows the relatively slow diffusivities of long-chain *n*-alkanes in the zeolite 5A structure to be investigated. Measurements were recently performed for *n*-hexane, and good agreement was observed for the results from NSE and PFG NMR spectroscopy.[6]

A characteristic of neutron scattering is the possibility to obtain the self-diffusivity by using hydrogenated molecules,

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which scatter incoherently, and the transport diffusivity in the case of coherent scatterers, such as deuterated molecules.[7] In NSE, a better signal is obtained with coherent scatterers. This is because spin-polarized neutrons are used, and one wants to recover as far as possible the initial polarization. When the sample contains hydrogen, the spin-incoherent scattering modifies the polarization of the incoming beam from $P$ to $-1/3P$, whereas a coherent scatterer leaves the polarization unchanged. This is the reason why we studied deuterated $n$-alkanes. Another advantage of the microscopic neutron-scattering technique is the possibility of deriving the transport diffusion coefficient, a quantity which is usually obtained from macroscopic measurements. This is because in coherent scattering, the intensity is related to pair correlation functions, so that one has access to density fluctuations in the adsorbed phase. The measured quantity is the normalized intermediate scattering function [Eq. (1)].

$$\frac{I(Q,t)}{I(Q,0)} = \exp(-D(Q)\,Q^2\,t) \qquad (1)$$

The values obtained at different times $t$ are normalized to the value measured at $t=0$. Experimentally, the neutron momentum transfer $Q$ is kept constant, and provided the length scale ($\approx 2\pi/Q$) is large enough, the collective diffusion coefficient $D(Q)$ which is derived becomes the macroscopic transport diffusivity $D_t$. Normalized intermediate scattering functions measured under the same experimental conditions for several $n$-alkanes at 475 K are shown in Figure 2. The data do not tend to unity at short times because of fast motion within the cages. Since a faster decay corresponds to a larger diffusion coefficient [Eq. (1)], a simple visual inspection of Figure 2 leads to the conclusion that the diffusivity increases with increasing chain length in the sequence $C_8 < C_{10} < C_{12}$. From measurements at two different $Q$ values, and by using a jump diffusion model,[6] the diffusion coefficients of the longer $n$-alkanes could be derived (Figure 1c).

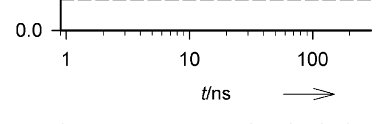

***Figure 2.*** Comparison between experimental and calculated normalized intermediate scattering functions for some $n$-alkanes in zeolite 5A at 475 K: $n$-octane (◆), $n$-decane (□), and $n$-dodecane (●); $Q = 0.2$ Å$^{-1}$. The dashed line represents the elastic contribution of the zeolite. The concentration of $n$-alkane was similar for all samples in that the number of $CD_x$ groups ($x = 2$ or 3) per cavity was the same (12). This ensures that a similar variation is obtained for the corrected diffusivities, after correcting from the thermodynamic factor, which is related to the driving force.

We find for $n$-alkanes in zeolite 5A that the diffusivity drops to a minimum at $C_8$, rises for $C_{10}$, has a maximum at $C_{12}$, and then decreases again for $C_{14}$. These experimental data are somewhat in contradiction with recent molecular simulations, which predict a maximum in zeolite 5A only for much longer chains.[8] However, several simplifications must be made in simulations on large systems, so that the computational requirements do not become prohibitive; for example, the cations and electrostatic interactions were ignored in reference [8]. Neutron spin echo measurements are planned on even longer $n$-alkanes to resolve the discrepancy between experiment and simulation.

The activation energies for diffusion were determined from measurements at different temperatures. An Arrhenius plot is shown in Figure 3. $C_{12}$ is more mobile than $C_8$ by a factor of 8.4 at 475 K, and by more than one order of magnitude at 436 K. The maximum in the diffusivities should be even more pronounced at 300 K. The finding that $E_a$ for $C_8$ (41 kJ mol$^{-1}$) is larger than that of $C_{12}$ (35 kJ mol$^{-1}$) supports the interpretation of our data in terms of the window effect. Our interpretation is shown schematically in Figure 4: a $C_8$ chain adopts a conformation that just fits in a cavity and sits in a deep potential well, whereas $C_{12}$ is too long to fit comfortably in a cage and adopts a conformation in which at least one end of the molecule extends through a window. The energy barrier (largely entropic) is thus much easier to cross for the longer molecule, and this leads to a higher diffusivity and lower activation energy. For $n$-alkanes longer than $C_{12}$, the diffusion coefficient decreases because of the higher molecular weight. Periodicity of diffusivity may exist for even longer $n$-alkanes, with a possible second minimum in the $C_{16}$–$C_{18}$ range.

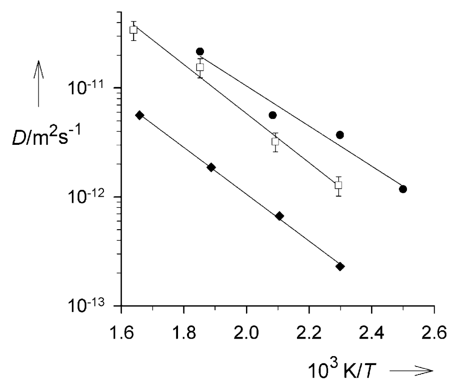

***Figure 3.*** Temperature dependence of the diffusion coefficients determined for some $n$-alkanes in zeolite 5A: $n$-octane (◆), $n$-decane (□), and $n$-dodecane (●). Typical error bars are shown.

This unexpected diffusion effect was not found in NaX zeolite, because the windows are too large (note that the diameters of the large cages in NaX and 5A are very similar). An increase in diffusion occurs in systems for which the sizes of the molecule and of the aperture between cavities are similar, and when the characteristic length scales of the molecule and of the cavity are comparable. In fact, anomalous

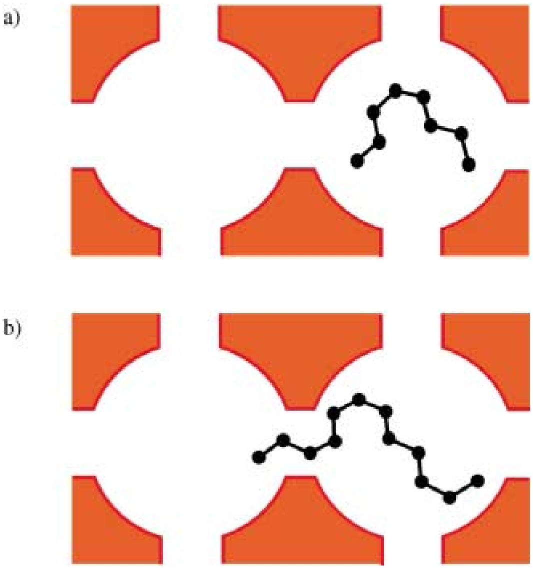

*Figure 4.* Schematic representation of the configuration of *n*-alkanes in zeolite 5A: *n*-octane just fits into a cavity (a), but one end of *n*-dodecane sits in a window between cages (b).

diffusion is not simply due to the size of the window, it depends both on the cage and window sizes. One could also look for a maximum in the diffusivity of branched alkanes in faujasite zeolites (X or Y), since the dimensions of the molecules and of the windows are comparable. The interplay between cages and windows may also affect the diffusion of molecules in porous materials other than zeolites, for example, in organic or inorganic membranes.

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