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Diffusivities of *n*-Alkanes in 5A Zeolite Measured by Neutron Spin Echo, Pulsed-Field Gradient NMR, and Zero Length Column Techniques

HERVÉ JOBIC
Institut de Recherches sur la Catalyse, CNRS, 2 ave. Albert Einstein, 62926 Villeurbanne, France

JÖRG KÄRGER AND CORDULA KRAUSE
Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany

STEFANO BRANDANI AND A. GUNADI
Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, England
s.brandani@ucl.ac.uk

A. METHIVIER
Institut Français du Pétrole, BP 311, 92852, Reuil-Malmaison, France

G. EHLERS, B. FARAGO AND W. HAEUSSLER
Institut Laue-Langevin, BP 156, 38042, Grenoble, France

DOUGLAS M. RUTHVEN*
Department of Chemical Engineering, University of Maine, Orono, ME, 04468, USA

Abstract. Diffusion of linear alkanes in 5A zeolite crystals has been studied by several different experimental techniques. In the range C_3–C_8 the diffusivity decreases regularly with carbon number (with a corresponding increase in activation energy) and there is good agreement between ZLC values and the data provided by the "microscopic" techniques (PFG NMR and Quasi-Elastic Neutron Scattering). At higher carbon numbers the agreement between the different techniques is less satisfactory, partly because of uncertainty in the thermodynamic correction factors. The microscopic techniques both show that the monotonic decrease in diffusivity does not continue beyond C_8. The self-diffusivities determined by PFG NMR remain essentially constant with some indication of a weak maximum at C_{10} while the transport diffusivities measured by the neutron spin-echo technique (NSE) show a clear maximum at C_{12}, reminiscent of the so-called "window effect" (Gorring, 1973).

Keywords: 5A zeolite, alkanes, ZLC, PFG NMR, neutron scattering, diffusion

Introduction

The problem of discrepancies between different methods of measuring intracrystalline diffusion in zeolites is now well known (Jobic, 2000; Talu et al., 1998; Kärger and Ruthven, 1992). In order to resolve this issue a collaborative research project has been initiated with the aim of making comparative diffusion measurements, for selected systems under similar conditions, by different experimental techniques. We report here

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*To whom correspondence should be addressed.

the first results of this project in which the diffusion of linear alkanes in 5A zeolites has been measured by NSE (neutron spin-echo), PFG NMR and ZLC techniques. These techniques span diffusion length scales from a few unit cells (for NSE) to the entire crystal (for ZLC).

Experimental Methods

N.S.E.

The neutron spin-echo technique is unique in that it allows direct measurement of *transport* diffusion on a microscopic scale (Jobic, 2000). The method depends on the determination of the Larmor precession angle of the neutron spin in a strong magnetic field of spatially varying intensity. Small changes in energy lead to decreased polarization and hence a reduction in the amplitude of the echo. The echoes are measured for different field integrals corresponding to different Fourier times. The NSE spectrometer at the Institut Laue-Langevin, where these measurements were carried out, can probe relatively long times (hundreds of nano-seconds) thus allowing the diffusion of relatively slowly moving species such as the medium chain length linear alkanes in 5A to be measured over distances corresponding to several unit cells. The measurements were made with the fully deuterated species since, in contrast to hydrogen, deuterium scatters neutrons coherently leading to a much stronger NSE signal.

PFG NMR

The pulsed field gradient NMR technique depends on measuring the decay in signal intensity arising from dephasing of the nuclear spins due to random (Brownian) motion in a spatially varying magnetic field. Detailed descriptions of the method and the underlying theory have been given elsewhere (Kärger and Ruthven, 1992). This technique yields the self-diffusivity under equilibrium conditions. The timescale (and therefore the length scale) of the measurement is determined by the interval between successive gradient pulses. By varying this interval it is in principle possible to vary the scale of the measurement from a few unit cells up to the dimensions of the zeolite crystal. However, the measurement must be completed within the relaxation time of the NMR signal. For the present systems (medium chain linear alkanes in 5A) relaxation times were relatively short and as a result the length scale of the measurements was limited to about 1 μm.

ZLC

The ZLC technique (Eic and Ruthven, 1988a; Ruthven and Brandani, 2000) depends on following the desorption of a small sample of adsorbent, pre-equilibrated at a uniform sorbate loading, and purged at a sufficiently high flow rate to ensure that the desorption rate is controlled by diffusion out of the crystal rather than by convective transport. This technique measures D_0, the limiting transport diffusivity at low loading and the diffusivity values are global averages over the entire crystal (or sample). For diffusion of various different hydrocarbons in silicalite it has been shown that the ZLC diffusivities are consistent with the values obtained by other macroscopic techniques such as the TEOM and, for the slower diffusing species, with direct gravimetric uptake rate measurements (Zhu et al., 2001).

A variant of the ZLC technique (tracer ZLC) based on the use of isotopically tagged species allows measurement of self-diffusivities as a function of loading, thus providing data which should be directly comparable with PFG NMR diffusivities (Brandani et al., 1995).

Relationships Between Diffusivities

The transport diffusivity (measured in the NSE experiments) is a concentration dependent quantity. It is related to the thermodynamically corrected diffusivity (D_0) by:

$$D = D_0(\partial \ell np/\partial \ell nq)_T \tag{1}$$

If the equilibrium isotherm is of Langmuir form this reduces to:

$$D = \frac{D_0}{(1 - q/q_s)} \tag{2}$$

where q_s is the saturation limit. In principle D_0 is also a function of loading but for many systems including linear alkanes in 5A this dependence is insignificant so that D_0 can be taken as constant and equal to the limiting diffusivity at zero loading.

The relationship with the self-diffusivity (D) is less straightforward. From simple microdynamic considerations one may argue that, since both transport and self-diffusion occur by the same basic mechanisms, D_0

and D must coincide in the low-loading limit. To obtain a relationship between these quantities at higher loadings requires a model for the diffusion process. The Maxwell-Stefan formulation leads to Paschek and Krishna (2001):

$$\frac{1}{D} = \frac{1}{D_0} + \frac{\theta}{D_{ij}} \tag{3}$$

where D_{ij} represents the mutual diffusivity in the Maxwell-Stefan formulation. When either $\theta \to 0$ or $D_{ij} \to \infty$ (no interference between diffusing molecules) $D \to D_0$, otherwise $D < D_0$. Since for these systems D_0 is essentially independent of loading (Doetsch et al., 1974), it follows that, if D is also independent of loading, D_{ij} must be large and therefore $D \approx D_0$.

It is shown below that for the medium chain alkanes in 5A the dependence of self-diffusivity on loading is quite weak so the assumption that $D \approx D_0$ should be a reasonable approximation. In comparing the diffusivities obtained by the three experimental techniques it is therefore logical to compare the PFG NMR self-diffusivities with the low loading diffusivities from ZLC and the thermodynamically corrected diffusivities from NSE.

Results and Discussion

Self-Diffusivities

The variation of self-diffusivity at 473 K (measured by PFG NMR) with carbon number is shown in Fig. 1. Recent measurements for n-hexane and n-octane are in good agreement with previously reported measurements for these species using different samples of 5A zeolite (Heink et al., 1992). The self-diffusivity decreases strongly with carbon number up to about C_7, but at higher carbon numbers it becomes more or less constant. Beyond C_8 the relaxation times are short, making accurate diffusion measurements difficult. Data obtained in replicate experiments with different samples show a good deal of scatter so it is difficult to establish the pattern of behavior with any confidence. The data appear to suggest a small minimum in the diffusivity at C_8 and a small maximum at C_{10} but the magnitude of the deviations from the mean value is not much greater than the experimental uncertainty. It may therefore be more logical to interpret these data as indicating that the self-diffusivity is approximately constant over the range C_7 to C_{14}.

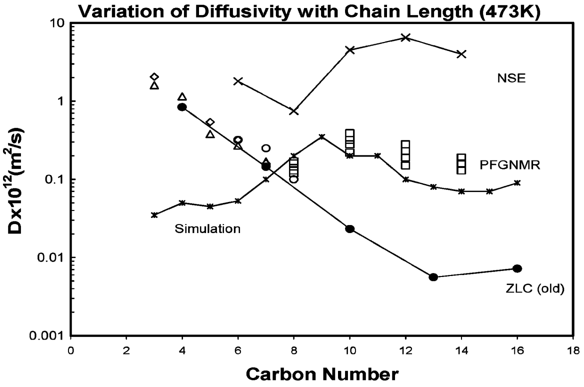

Figure 1. Variation of diffusivity with carbon number (at 473 K). NSE (D), x; ZLC (D_0) (Eic and Ruthven, 1988b), ●; ZLC (recent data) ○; PFG NMR (D) data of Heink et al. (1992) at 1 mol/cage Δ, and 2 molecules/cage ◇. Recent data (1 molecule/cage), □. Molecular simulation (Dubbeldam and Smit, 2003).

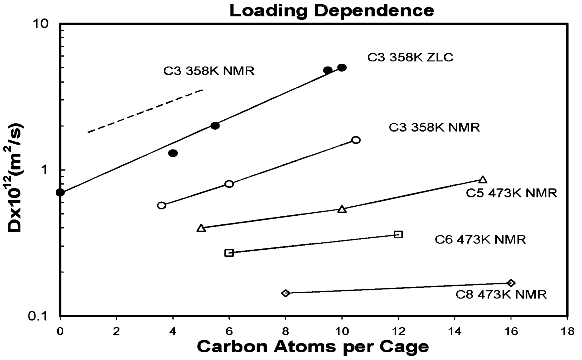

Figure 2. Variation of self-diffusivity with loading for linear alkanes in 5A Zeolite. PFG NMR data of Heink et al. (1992); ○, □, Δ. New data ◇. Earlier data of Kärger and Ruthven (1981) for propane at 358K - - - -. TZLC data of Brandani et al. (1995).

As may be seen from Fig. 2 the self-diffusivity increases with loading. Measurements for propane were made by both PFG NMR (Heink et al., 1992; Kärger and Ruthven, 1981) and tracer ZLC (Brandani et al., 1995) techniques and the results show reasonably good agreement. The magnitude of the variation of self-diffusivity with loading decreases with increasing carbon number so that for C_8 (and higher homologs) the self-diffusivity becomes almost independent of loading.

Comparison with Molecular Simulations

The variation of self-diffusivity with chain length for diffusion of linear alkanes in the silica analog of LTA

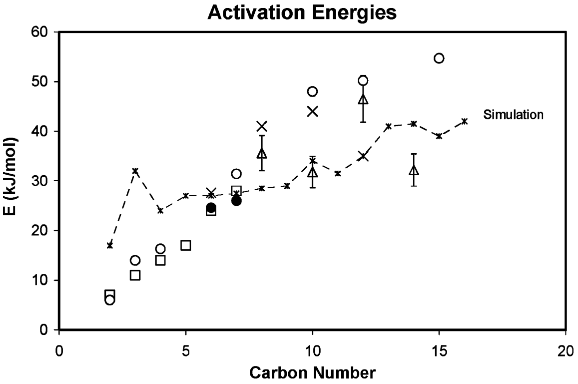

Figure 3. Variation of activation energy with carbon number o, old ZLC (D_0); ● recent ZLC data; □, Δ PFG NMR (D); *x* NSE (D); *molecular simulations (Dubbeldam and Smit, 2003).

zeolite has recently been predicted by Dubbledam and Smit using a combination of transition state and CBMC methods (Dubbeldam and Smit, 2003). Over the range C_7 to C_{14} the predicted diffusivities, shown in Fig. 1, lie remarkably close to the PFG NMR data, even replicating the small maximum at C_9–C_{10}. The activation energies (for C_7–C_{14}) are also similar (see Fig. 3) but for lower carbon number (C_3–C_6) the predicted diffusivities lie well below the experimental values and the predicted activation energies are much too large. The Henry constants and heats of adsorption calculated from the energy profiles used in the simulation are very different from the experimental values for 5A zeolite. One cannot therefore exclude the possibility that the remarkable agreement between theory and experiment (over the range C_7–C_{14}) may be fortuitous.

Comparison of Self- and Transport Diffusion

Up to C_8 the ZLC (D_0) and PFG NMR (D) values are in good agreement. Recent ZLC measurements for C_6–C_8 agree well with the earlier data (Eic and Ruthven, 1988b). However, the ZLC data suggest that the decreasing trend of diffusivity with carbon number continues beyond C_8 whereas the PFG NMR data suggest that the self-diffusivity becomes approximately constant in this region, leading to a substantial discrepancy at higher carbon numbers. The earlier ZLC measurements were among the first to be carried out by this technique and at that time the experimental system had not been fully optimized. The measurements for the higher carbon numbers should therefore be repeated since, for strongly adsorbed species, there is always a possibility of intrusion of extracrystalline mass transfer resistance and/or equilibrium constraints.

The comparison between PFG NMR and NSE data (see also Jobic et al., 2004) is less straightforward. The NSE data show a well defined maximum in the transport diffusivity at C_{12} whereas the PFG NMR data show a weaker maximum in the self-diffusivity at C_{10}. Both these data sets are reminiscent of the so-called “window effect”, originally suggested by Gorring (1973) to explain the unusual pattern of variation of apparent diffusivity with carbon number for linear alkanes in zeolite T. Although the validity of Gorring’s original data has been called into question by more recent experimental studies which show a monotonic decrease in transport diffusivity over the relevant range of carbon number (Cavalcante et al., 1995; Magalhaes et al., 1996) the possibility of a local maximum in the variation of diffusivity with carbon number, arising from a match between the lattice parameter and the length of the diffusing molecule, remains an intriguing theoretical possibility which has attracted much attention from theoreticians (see for example Runnebaum and Maginn, 1997; Tsekov and Smirniotis, 1998; Ghorai et al., 2003; Dubbeldam and Smit, 2003). The NSE and PFG NMR data reported here provide the first direct *microscopic* experimental evidence of such an effect. It is possible that the differences between the NSE and PFG NMR data can be accounted for by the thermodynamic correction factor. A more detailed analysis of these data will therefore require accurate equilibrium isotherms at the experimental temperature.

Activation Energies

The variation of diffusional activation energy with carbon number is shown in Fig. 3. The activation energy increases regularly with carbon number up to about C_8 reflecting the monotonic decline in diffusivity in this region. At higher C numbers the data become quite scattered probably as a result of the poor measuring conditions (for PFG NMR) and the limited accessible temperature range. It may be that beyond C_8 the activation energy is almost constant but because of the large scatter of the data this is by no means certain. The activation energies for the ZLC and NSE measurements are very similar to the PFG NMR values especially at lower carbon numbers where the values are more reliable.

Conclusions

The results of this study lead to a somewhat confusing picture. At low carbon numbers both self-diffusivities and corrected transport diffusivities decrease regularly with carbon number and the activation energies show a corresponding increasing trend. In this region there is excellent agreement between PFG NMR and ZLC data, as to both the magnitude of the diffusivities (and the corresponding activation energies) and their trends with carbon number. Furthermore, for propane, the loading dependence of the self-diffusivity, as measured by PFG NMR and tracer ZLC, also shows good quantitative agreement. However, beyond C_8 the agreement becomes poor since the PFG NMR data suggest that the self-diffusivity becomes almost constant whereas the ZLC data show a continuing decline before leveling off above C_{13} at a much lower value. The NSE transport diffusivities are substantially greater than the PFG NMR self-diffusivities but much of this difference is attributable to the thermodynamic correction factor. The length scale of the ZLC measurements, which were made with relatively large 5A crystals (7–16 μm) is substantially greater than that of the PFG NMR self-diffusivity measurements so it is certainly possible that the difference in the diffusivities at higher carbon numbers may arise from the influence of structural defects which becomes progressively more important over longer distances and for larger molecules (Jobic et al., 2003; Vasenkov and Kärger, 2002). However, it is also possible that the ZLC measurements for the higher carbon numbers were impacted by extracrystalline resistance and /or equilibrium limitations.

For C_7–C_{14} there is remarkably close agreement between the experimental PFG NMR diffusivities and the values predicted by molecular simulation for the idealized pure silica analog of LTA zeolite.

Nomenclature

D	diffusivity
D_0	"corrected" diffusivity
D_{ij}	mutual diffusivity (in Maxwell-Stefan model)
D	self-diffusivity
p	partial pressure of sorbate
q	sorbate loading
q_s	saturation limit
θ	fractional saturation ($= q/q_s$)

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