

## Concentration Dependence of Transport and Corrected Diffusivities of n-Hexane in Silicalite Measured by QENS

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### 1. Introduction

Separation induced by kinetic effects using zeolite as a shape selective adsorbent is of great industrial concern. The control of diffusion process, requiring a precise knowledge of self-, transport and corrected diffusivities ( $D_{self}$ ,  $D_t$  and  $D_C$ , respectively), is essential for the design of industrial applications.  $D_{self}$  and  $D_t$  are usually measured directly by microscopic and macroscopic methods, respectively, while  $D_C$  is extracted from the macroscopic quantity  $D_t$  using the Darken equation,  $D_t(\theta) = D_C(\theta) \partial \ln f / \partial \ln \theta$ . Those three diffusivities depend on loading  $\theta$  and become only equal when  $\theta \rightarrow 0$ . However, longstanding discrepancies subsist on the diffusivity values measured by different techniques: indeed, different mass transfer resistances arise within the crystal since spatial observation ranges differ by several orders of magnitude. Moreover, controversies arise on the frequent, but erroneous, assumption of the independence of  $D_C$  vs. loading that allows to relate  $D_{self}$  to  $D_t$ . Therefore, techniques that can provide multiple diffusion coefficients are of major interest. Besides atomically detailed simulation, Quasi-Elastic Neutron Scattering (QENS) is the only experimental technique so far that succeeds in estimating both  $D_{self}$  and  $D_t$  by using hydrogenated and deuterated compounds [1].

In this letter, the loading dependency of the transport and corrected diffusivities of linear hexane in silicalite close to saturation (8 molecules / u.c) is investigated by QENS. Using  $D_{self}$  also measured by QENS, the self-exchange coefficient  $\mathcal{D}_{11}(c)$  arising from the Maxwell-Stefan formulation for single component and the  $\mathcal{D}_{11}(\theta) / D_C(\theta)$  ratio giving information about the influence of correlation effects, are calculated [2].

### 2. Results and discussion

The experiments were performed on hydrogenated and deuterated n-hexane at the Institut Laue-Langevin, Grenoble, France, by taking a 6.27 Å incident wavelength. Details of sample preparation and  $D_t$  calculations can be found in [3].  $D_C$  was estimated using the thermodynamic factor based on a single-site Langmuir adsorption model.

As shown in Fig1 the transport diffusivity remains constant up to 5 molecules/u.c. after which it slightly decreases. The corrected diffusivity decreases linearly with increasing loading, diminishing by two orders of magnitude over the entire range of loading investigated. This behaviour of  $D_C$  confirms the deviation from the Darken

approximation observed experimentally for ethane [3], and is different from the atomically simulated behaviour of methane that remains constant [4] under the same conditions.  $D_C$  extracted from macroscopic methods remains 1 or 2 order of magnitude lower but a quantitative comparison cannot be rigorous, as they are determined at various experimental conditions. Moreover, contrary to QENS they exhibit an increase for  $\theta < 4$  molecules/u.c [5].

The calculation of  $D_{II}(\theta)$  based on diffusivities provided by the same experimental technique has never been done so far.

For the linear hexane, activation energies of around 7.0 and 5.0  $\text{KJmol}^{-1}$  are obtained for transport (1 molecule/u.c) and self-diffusion (2 molecules/u.c), respectively. This is in agreement with molecular dynamics simulation [6].

### 3. Conclusions and perspectives

Transport and corrected diffusivities of linear hexane in silicalite were measured by QENS.  $D_t$  remains constant up to 5 molecules/u.c. and then exhibits a slight decrease.  $D_C$  was found to decrease linearly with increasing loading. The  $D_C$  loading dependence confirms that the approximation of the Darken equation does not apply for the linear hexane in MFI-type zeolites. A Kinetic Monte Carlo (KMC) study based on a lattice model and jump frequencies provided either by experimental or other theoretical techniques is currently developed. It will allow to simulate experimental behaviours of  $D_{self}$  and  $D_C$  regarding loading and topology, as well as the nearest neighbours' influence that is considered by implementing a  $\delta E$  in the energy barrier to take into account repulsive or attractive effects [7].

### References

- [1] H. Jovic, J. Kärger, M. Bee, Phys. Rev. Lett. 82 (1999) 4260
- [2] A.I. Skoulidas, D.S. Sholl, R. Krishna, Langmuir 19 (2003) 7977
- [3] D.S. Sholl, H. Jovic, S. Chong, M. Plazanet, Chem Phys Lett. 408 (2005) 157-161
- [4] E.J. Maggin, A.T. Bell, D.N. Theodorou, J. Phys. Chem. 97 (1993) 4173-4181
- [5] A.O. Koraibkina, A.M. de Jong, E.J.M. Hensen, R.A. van Santen, Micropor. Mesopor. Mater. 77 (2005) 119-129
- [6] E.J. Maggin, A.T. Bell, D.N. Theodorou, J. Phys. Chem., 100 (1996) 7155-7173
- [7] R. Krishna, D. Paschek, Chem. Phys. Lett. 342 (2001) 148-154

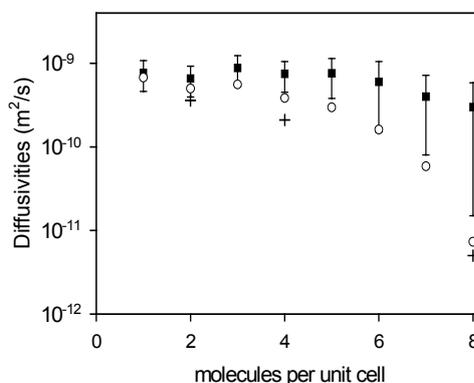


Fig1: Loading dependence of n-hexane diffusivities in silicalite: (■)  $D_t$ , (O)  $D_C$  and (+)  $D_{self}$