

# diffusion-fundamentals

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## A Remarkable Non-Monotonical Chain-Length Dependence: Diffusion of n-Alkanes in Zeolites LTA

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### 1. Introduction

While in the case of the bulk fluid and in large- and medium-pore zeolites, the diffusivities of n-alkanes are found to decay essentially monotonically with increasing chain length, in zeolites LTA (notably in NaCaA) a remarkable deviation from this pattern is observed. Applying different measuring techniques, viz. the spin-echo technique of quasi-elastic neutron scattering (NSE), pulsed field gradient (PFG) NMR and zero length column (ZLC) measurements, an international research collaboration has been initiated to compare how these deviations are reflected by the different techniques.

### 2. Results and discussion

Fig. 1 provides an overview of the diffusivity data obtained with the different measuring techniques. Two prevailing features are observed: (i) The measured diffusivities diverge, with the largest values for NSE and the smallest ones for ZLC. (ii) In all techniques (albeit for different chain lengths) the monotonical decrease with increasing chain lengths for small carbon numbers is found to switch over into a range where the diffusivity is found to be essentially constant (PFG NMR and ZLC) or to exhibit even a pronounced maximum (NSE) [1].

Item (i) may be referred to the fact that the different techniques cover the molecular diffusion paths over different distances. They increase just in the same sequence as the diffusivities decrease. Hence, the differences in the absolute values may be explained by the existence of internal barriers (and additional resistances at the crystal surfaces), which become the more dominant, the larger are the displacements.

The coinciding trend in a notable deviation from a further monotonical decrease with increasing chain lengths (item (ii)) may be rationalized in the following way. Due to energetic and entropic reasons, positions within the cavities are occupied by the individual elements of the n-alkane chains with notably higher probability than those in the "windows" between these cavities. For small molecules this represents a barrier. If, however, the n-alkanes are too large to fit into one cavity, a part of the chain has anyway to be positioned in a window. Hence, at some critical chain length the rate of molecular propagation may in fact be anticipated to increase.

### 3. Conclusion

Since the methods applied differ in both the observed diffusion path lengths and state of diffusion, viz. self- and transport diffusion, future studies have to clarify whether the observed trends of the diffusivities in deviating from the monotonical decay may be attributed to identical microdynamic phenomena.

### References

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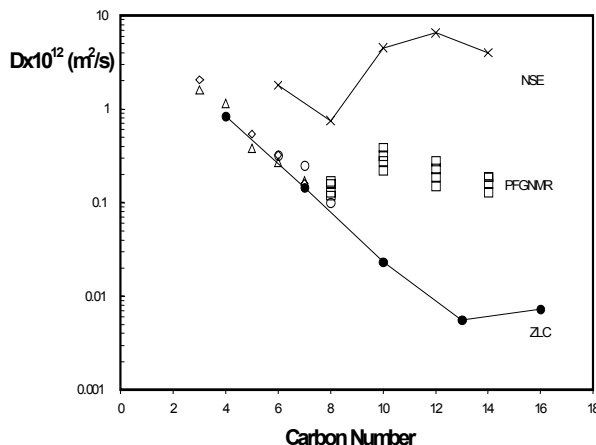


Figure 1. Variation of diffusivity with carbon number (at 473K). NSE x [1]; ZLC ● [2]; ZLC ○ [3]; PFG NMR data at 1 mol/cage Δ, and 2 molecules/cage ◇ [4], recent data (1 molecule/cage) □.