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Assessing Details of Molecular Motion in Nanopores by Combining Different Microscopic Techniques

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1. Introduction

The introduction of optical microscopic techniques, like interference microscopy and infrared micro-imaging, to diffusion studies in nanoporous materials means a decisive breakthrough as shown in the article of Binder et al. in this volume. With the direct observation of the transient concentration profiles, such fundamental details on the mass transfer like the transport diffusivity, the surface permeability and the sticking (or entering) probability of the guest molecules are accessible. In this work, we want to demonstrate that even further information on the molecular motion in the nanopores may be derived from the experimental data.

For this purpose we study the mass transfer of the guest-molecule propane in the host-system MOF Zn(tbip). The transport parameters were determined by analysing the concentration profiles recorded by interference microscopy and infrared micro-imaging as explained in refs. [1, 2]. The determined Maxwell-Stefan, transport and self-diffusivity are shown in figure 1.

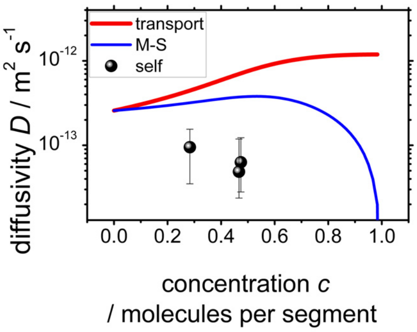

Figure 1: Maxwell-Stefan (M-S), transport and self-diffusivity of propane in MOF Zn(tbip), taken from ref. [1].

2. The probability of molecular passage and the exchange coefficient

Comparing the size of the one-dimensional nanopores in MOF Zn(tbip) with the size of propane, one may expect that the molecules are not able to pass each other in the pore space, resulting in single-file diffusion [3]. The single-file behaviour leads to an exchange process which is $N\theta/(1-\theta)$-times slower than the uptake (or release) process [3]. θ denotes the occupancy (equals the relative concentration) and N the number of pore segments in this linear pore space. With an occupancy of $\theta = 0.5$, a crystal length of $l \approx 100$ µm and a segment length of $\lambda = 0.8$ nm, the single-file self-exchange process would last about 100,000-times longer than the uptake. In the experiments, a self-diffusivity one order of magnitude smaller than the transport diffusivity was found. Therefore, deviations from the single-file behaviour have to occur; in other words the molecules are able to pass each other.

The passage rate Γ of a particular pair of adjacent molecules is related to the self- (or tracer) diffusivity D_{self} by the simple random-walk expression

$$D_{\mathrm{self}} = l^2\,\Gamma \quad (1)$$

where l denotes the mean distance between adjacent molecules which can be estimated by $\lambda\ /\ \theta$. With the assumption that a jump attempt towards an occupied segment is only successful with a probability p, the passage rate Γ may be expressed by

$$\Gamma = p \times \frac{(1-\theta)}{2\tau} \quad (2)$$

with the mean time τ between two jump attempts. Combining both equations yields

$$D_{\mathrm{self}} = \frac{\lambda^2}{2\tau}\frac{p\times(1-\theta)}{\theta^2} = D(0)\frac{p\times(1-\theta)}{\theta^2} \quad (3)$$

from which one obtains passage probabilities of $p = 5.5 \times 10^{-2}$ and 8.8×10^{-2} for $\theta = 0.28$ and 0.48, respectively [1]. A solid statement whether the molecular passage happens at crystal defects or in the defect-free pore space is, however, not yet possible.

The correlation of the molecular jumps may be estimated by [4]

$$D_{\mathrm{self}}{}^{-1} = D_{\mathrm{M\text{-}S}}{}^{-1} + \theta \times D_{\mathrm{exchange}}{}^{-1} \quad (4)$$

yielding an "exchange coefficient" D_{exchange} of 3.8×10^{-14} m^2 s^{-1} and 3.6×10^{-14} m^2 s^{-1}, respectively. The "exchange coefficient" is smaller than the self-diffusivity indicating a strong correlation between the jumps of the molecules.

3. Conclusion

By comparing the Maxwell-Stefan and the self-diffusivity at different loadings, we attained further information on the molecular motion in the nanopores, namely the probability that two molecules may pass each other and the exchange coefficient. The molecules are able to pass each other in the nanopores, but only with a small probability of roughly 7 %. Furthermore, a strong correlation between the molecular jumps was verified, which is typical for one-dimensional channel systems.

4. References

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