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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Faster by Opposing the Stream

Christian Chmelik[1], *Helge Bux*[2], *Jürgen Caro*[2], *Lars Heinke*[1, 3], *Florian Hibbe*[1], *Tobias Titze*[1], *Jörg Kärger*[1]

[1]University of Leipzig, Faculty of Physics and Geosciences, Department of Interface Physics, 04103 Leipzig, Germany, E-Mail: kaerger@physik.uni-leipzig.de

[2]Leibniz University Hannover, Institut für Physikalische Chemie und Elektrochemie, 30167 Hannover, Germany

[3]Lawrence Berkeley National Laboratory, Materials Science Division, Berkeley, California 94720, United States

1. Introduction

Diffusion, i.e. the irregular movement of molecules, is quantified by measuring the rate of molecular fluxes in the direction of falling concentration. In contrast to intuition, considering methanol diffusion in a novel type of nanoporous material (MOF ZIF-8) this rate has now been found to be enhanced rather than slowed down by an opposing flux of labelled molecules [1,2]. In terms of the key quantities of random particle movement, this result means that the self-diffusivity exceeds the transport diffusivity. It is rationalized by considering the strong inter-molecular interaction and the dominating role of inter-cage hopping in mass transfer in the systems under study.

2. Results and Discussion

Mimicking the structural properties of SOD-type zeolites, ZIF-8 consists of a cubic arrangement of large cavities separated by small “windows”, with respective diameters of 1.16 nm and 0.34 nm. As guest molecules, methanol, ethane and ethanol were compared.

Figure 1b summarizes the transport diffusivities and self-diffusivities of methanol determined in IR microscopy (IRM, [1]) measurements from molecular uptake over different loading steps and from tracer exchange at different loadings [1,2]. Over essentially the total range of concentrations the rate of molecular uptake is notably exceeded by the rate of tracer exchange, i.e. $D_{\mathrm{self}} > D_{\mathrm{T}}$!

The explanation of this finding necessitates the inclusion of a mechanism which over-compensates the effect of the space confinement. Finiteness of pore space accelerates transport diffusion in comparison with self-diffusion. To date all microscopic diffusion studies confirm this “finite-size effect” of pore space: the transport diffusivities in nanoporous solids are found to be larger than or, at least, equal to the self-diffusivities. In the present case hydrogen bonding between the methanol molecules leads to a strong attractive interaction of the diffusants, leading to the observed retardation rather than acceleration of transport diffusion in comparison with self-diffusion.

A more fundamental discussion is based on the Maxwell-Stefan model for diffusion in nanopores. Since the host system under study consists of a pore network, in which the diameters of the interconnecting “windows” are of the order of the diffusing molecules, self- and transport diffusion are found to be exclusively related to each other by the inverse “thermodynamic factor” ($1/\Gamma$): $D_{\mathrm{self}} \approx D_0 = D_{\mathrm{T}} \cdot \partial \ln c / \partial \ln p = D_{\mathrm{T}} / \Gamma$.

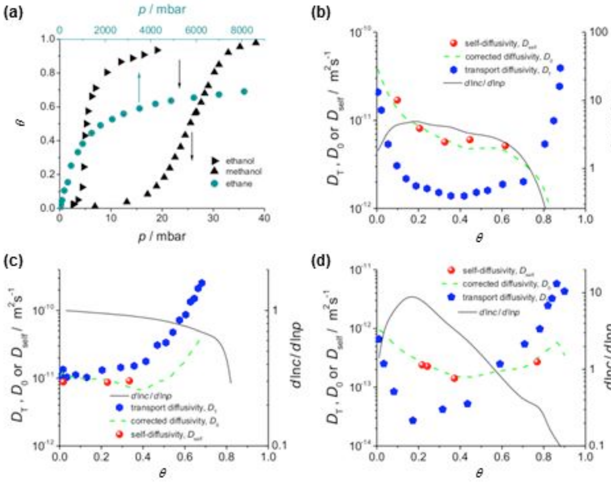

Fig. 1: Methanol, Ethane and Ethanol in ZIF-8 at 298 K. (a) The adsorption isotherm of ethane (upper ordinate scale) shows a usual (“type I”) behaviour, whereas the isotherms of methanol and ethanol (lower ordinate scale) exhibit a pronounced S-shape (“type III”). All isotherms were normalized to reach an occupancy of $\theta = 1$ at saturated vapor pressure. Loading dependence of transport (D_{T}), corrected (D_0) and self-diffusivity (D_{self}) of (b) methanol (MeOH), (c) ethane and (d) ethanol (EtOH). The full lines show the inverse thermodynamic factor as obtained from (a).

In contrast to the vast majority of diffusion studies with porous materials, the thermodynamic factor $\Gamma = \partial \ln p / \partial \ln c$ is found to be smaller than 1 (except for loadings $\theta > 0.8$). In Fig. 1a, this behaviour may be easily identified as a consequence of the (towards the ordinate) concave shape of the methanol adsorption isotherm. Such isotherms are referred to as type III isotherms and are well known to occur if the guest-guest interaction notably exceeds the guest-host interaction. Our first, intuitive speculation about the mechanism which may make molecular self-diffusion in nanopores faster than transport diffusion is thus nicely confirmed by the shape of the observed isotherm!

Our conclusions are found to be totally confirmed by complementary measurements with ethane and ethanol [1,2]. Ethane is a non-polar molecule and pronounced attractive interactions as observed with methanol may be excluded. Indeed, the adsorption isotherm exhibits a type I shape (Fig. 1a) and the diffusivities show the “normal” trend in the diffusivities: D_{T} is always larger or at least equal to D_{self} (Fig. 1c). For ethanol we note an interesting hybrid behaviour: methanol-like for loadings $\theta < 0.6$, but ethane-like for loadings $\theta > 0.6$ (Figs. 1a,d).

References

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