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

Surface Permeabilities: Entering an Unexploited Field by Means of Interference Microscopy

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1. Introduction

Coordination polymers - also known as metal-organic frameworks (MOFs) - are promising for applications in catalysis and gas storage. Transport through the pores of these materials occurs mainly by diffusion and often affects or even controls the overall rate of the process. Therefore, a detailed understanding of the diffusional behaviour in porous media and its complexities is more than essential for the design and optimization of the metal-organic framework materials. While intraparticle diffusion has been in the focus of numerous publications, so far the surface permeabilities have remained out of quantitative consideration - in contrast to their relevance in nano-technology and in related fields of life sciences and medicine. With the introduction of interference microscopy (Fig. 1), this deficiency may now be overcome.

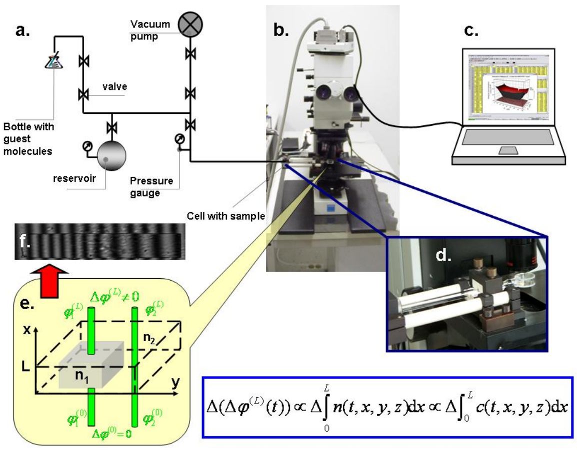

Figure 1: Schematices of diffusion measurement by interference microscopy (DIF)
a. Schematical drawing of the vacuum system; **b.** Interference microscope and the cell with the sample placed underneath its lenses; **c.** Computer connected to the camera for further analysis of the data; **d.** The cell with the sample under magnification; **e.** Schematical drawing of the principle; **f.** Interference pattern of an investigated crystal; The mathematical relation on the bottom side of the figure shows the proportionality between the change of intracrystalline concentration and of phase-difference between the light beams.

2. Transient experiments with Zn(tbip) crystals

Only very recently, crystals of type Zn(tbip) (group of Prof. J. Li, Rutgers University, USA) as novel members of the MOF family proved to be stable enough to allow the essentially unlimited repetition of adsorption-desorption runs with complete reproducibility. This extraordinary quality of the material allowed the measurement of surface permeabilities under variation of guest sizes, guest concentrations and the type of the experiments, namely equilibrium and non-equilibrium.

3. Conclusion

The diffusion studies by means of interference microscopy have revealed that there is a concurrence of the trends of surface permeabilities with the trends of the diffusivities. Furthermore, diffusivities measured for different specimens were found to vary less than 20%, whereas the surface permeabilites were different by factors up to 2 (Fig. 2) [1, 2]. Such observations show that the processes of diffusion and permeation are closely related and provide first insight into the nature of the surface resistances of the systems under study.

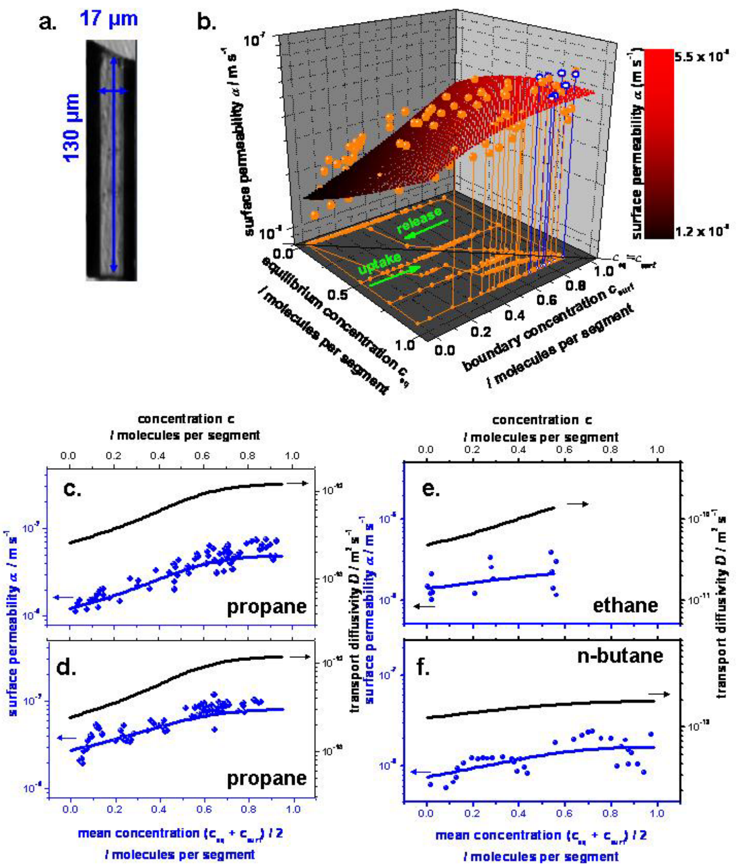

Figure 2: **a.** The crystal under study; **b.** Surface permeability as a function of the boundary and equilibrium concentration of propane; **c. –f.** Concentration dependencies of transport diffusivities and surface permeabilities (**d.** refers to another specimen of the sample).

References

[1] D. Tzoulaki, L. Heinke, W. Schmidt, U. Wilczok, J. Kärger, Angew. Chem. Int. Ed., 2008, 47, 3954-3957

[2] L. Heinke, D. Tzoulaki, C. Chmelik, et al. Phys. Rev Lett 102 (2009) 065901