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Diffusion in Hierarchical Pore Systems

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1. Introduction

With the advent of ordered mesoporous materials with hierarchically organized pore structures, many fundamental questions concerning the behaviour of confined fluids can now be addressed experimentally. Since they are promising materials for practical applications in catalysis, separation and adsorption, knowlegde of diffusion properties of such structures is of quintessential importance for their rational use.

In this work, transport properties of fluids confined to a silica material with an ordered, bimodal pore structure are studied by means of pulsed field gradient nuclear magnetic resonance (PFG NMR).

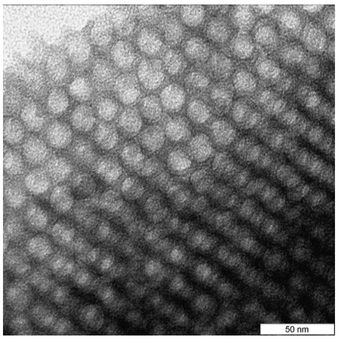

Fig.1. TEM image of PIB-IL material. The white regions show ordered spherical pores with a diameter of about 20 nm. The matrix as well contains cylindrical mesopores with a diameter of about 3 nm, interconnecting the spherical pores.

2. Experiment

The porous material used in this work (see Fig. 1), here referred to as PIB-IL, has been produced by a templating method. The resulting structure consists of spherical pores with a diameter of about 20 nm connected through worm-like cylindrical mesopores with a diameter of about 2-3 nm [1]. For further experimental studies, the porous material has been introduced into an NMR glass tube and outgased. By connecting the NMR tube to a big buffer volume with a vapour of the fluid under study, we had the possibility to perform NMR experiments with the PIB-IL sample in contact with the gas at certain pressure P. Thus, by measuring the signal intensity of the free induction decay signal, we had access to the amount adsorbed by the porous material (sorption isotherms). Simultaneously, more sophisticated NMR experiments yielded information on the fluid transport properties, such as molecular diffusivity [2].

Fig. 2 demonstrates the results of such measurements. It shows the relative amount adsorbed and the diffusivities of cyclohexane as a function of the relative external gas pressure P/P_s (P_s is the saturated vapour pressure) on the adsorption and desorption branches. The measurements have been performed at room temperature. First of all, the experimental results reveal a very broad adsorption hysteresis, pointing to a strong pore-blocking effect, which notably shifts the evaporation transition in the big spherical pores.

Secondly, the hysteresis in the amount adsorbed is accompanied by a hysteresis in the molecular diffusivities.

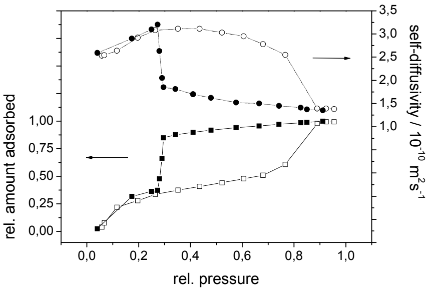

Fig. 2: The relative amount adsorbed (bottom) and self-diffusivities (top) of cyclohexane in PIB-IL material at 297 K as a function of relative pressure P/P_S. Open and filled symbols refer to adsorption and desorption branches, respectively.

The origin of the diffusion hysteresis has already been discussed in detail [2] and is referred to the fact that diffusivities in the gas-filled and liquid-filled regions are different. Thus, the measured diffusivities become directly related to the state of the fluid phase in the pores [3]. The well-defined, very peculiar organization of the pore structure of the material used allows, to quantitatively correlate the experimental results with the theoretical predictions.

In the present contribution, two different transport regimes will be considered. First, we analyze the diffusivities measured at full saturation of the pores with the liquid. The predictions of different models predicting long-range self-diffusivities in such structures will be compared to the experimental results [4, 5]. Another regime of interest is when only the small, worm-like mesopores are filled by the capillary-condensed phase, while the spherical pores contain multi-layered adsorbed molecules on the pore walls and vapour phase in the pore interiors.

3. Conclusions

Nuclear magnetic resonance has been applied to study adsorption and diffusion properties of fluids in hierarchically organized mesoporous material. It is found that the peculiar pore structure leads to a broad adsorption hysteresis. In parallel to adsorption hysteresis, the experiments also reveal hysteresis in the diffusivities of the confined fluid. Theoretical models capturing the most essential features of molecular transport under our experimental conditions are successfully applied to explain the experimental results.

References

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