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Adsorption Hysteresis in Nanopores: Options to a Comparative Study Using Nuclear Magnetic Resonance and Computer Simulation Methods

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1. Introduction

The behavior of fluids confined in porous materials can be very different from that in the bulk state. One example of this is the adsorption hysteresis in mesoporous materials, the origin of which is still controversially discussed in the literature. In the present work, this problem is experimentally addressed with aid of nuclear magnetic resonance (NMR) spectroscopy, that allowed us to follow the details of molecular dynamics in pores in the region of the adsorption hysteresis [1, 2].

2. Diffusivity hysteresis in mesopores

NMR spectroscopy provides unique possibilities to noninvasively probe different properties of adsorbate molecules in porous materials. In this study, adsorption and molecular self-diffusion of cyclohexane adsorbed in Vycor porous glass were simultaneously measured as a function of the external gas pressure. Importantly, dependence of the effective self-diffusion coefficient D_{eff} of intraporous liquid on the gas pressure was found to exhibit a hysteretic behaviour similar to that for the adsorption isotherm. This is demonstrated in Fig. 1, where D_{eff} and the pore filling factor θ (the adsorption) are shown as a function of the relative pressure $z=P/P_s$ (P_s is the saturated vapour pressure). The diffusivity hysteresis clearly points out a difference in character of the pore filling at equal vapour pressures attained during adsorption and desorption. It is worth noting that such hysteresis we have observed for a variety of porous materials with different pore morphology. Thus, the molecular motion, which is sensitive to microstructural details of the adsorbed phase distribution along a pore volume, may be considered as a new experimentally accessible parameter for probing the adsorbate state under metastable conditions.

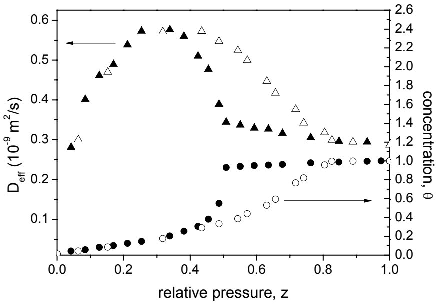

Fig. 1. The pore filling factor θ (circles) and the self-diffusion coefficients D_{eff} (triangles) for cyclohexane in Vycor porous glass as a function of the relative vapour pressure z measured on the adsorption (open symbols) and the desorption (filled symbols) branches.

3. Adsorption kinetics

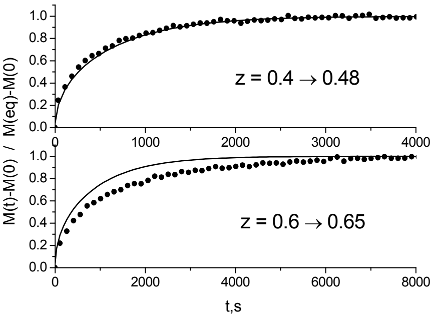

Fig. 2. Normalized concentration equilibration curves (circles) measured during adsorption of cyclohexane in Vycor porous glass out of (upper figure) and in (lower figure) the region of the hysteresis. The pressure steps are indicated in the figures. The lines show the expected relaxation within the model of diffusion-controlled equilibration.

The existence of metastable states should consequently lead to a specific response of the system to a change of the external parameters. In Fig. 2 we present two typical concentration relaxation curves obtained after a step change of the gas pressure. The lines show the functions calculated under the reasonable assumption that the uptake of the adsorbate into the porous glass is solely controlled by diffusion [3]. In the calculations, the measured diffusivities of Fig. 1 have been used. The most prominent result is that outside the hysteresis region the diffusion-limited model nicely fits the experimental data, while in the hysteresis region the relaxation slows down with respect to the predicted one. The latter suggests that the system becomes trapped in metastable states of local free energy minima, which relax via an activated barrier crossing process. This picture is consistent with computer simulation studies performed for a model porous systems of similar morphology [4, 5]. We consider the development of NMR methodologies for the detection of the characteristics of the local density fluctuations as a most challenging task of further investigations.

4. Conclusion

The use of new experimental methods providing information on the microscopical level may significantly contribute to understanding the adsorption hysteresis phenomena. Our preliminary studies using NMR spectroscopy reveal that this approach provides unique information on the adsorbate state and its dynamical properties in mesopores [1, 2]. The comparative analysis of the experimental data with results of computer simulations may yield new insight into the physics of metastable states under mesoscale confinements.

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