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

Assessing the Pore Critical Point of the Confined Fluid by Diffusion Measurement

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1. Introduction

Supercritical fluids (SCF) represent a special class of fluids with physical properties typical for both liquids and gases. With high densities as in the liquid state but, at the same time, possessing dynamical properties typical of gases (high diffusivity, low viscosity), these fluids have become a powerful tool of modern chemical industry. The use of SCF in such processes like heterogeneous catalysis, preparation of novel mesoporous materials, separation, etc., may not only enhance their productivity but also leads to completely new technological solutions and material properties.

2. Experimental method and sample preparation

In this study, by means of the pulsed field gradient NMR technique we investigated diffusion properties of confined n-pentane molecules undergoing a phase transition to the supercritical state within mesopores [1, 2]. Two porous glass materials have been used as host systems: Vycor particles of about 500 µm size having an internal mesoporous structure with a mean pore diameter of about 5 nm and ERM FD121 with particles of 140-200 µm size and of a pore diameter about 15 nm.

3. Results

The measured diffusivities of the bulk fluid and of the fluid in the pores are found to increase with increasing temperature following an Arrhenius law [3], with a difference in the absolute values caused by the tortuosity of the porous space (Fig. 1).

As expected, for the bulk fluid the transition to the supercritical state takes place at the bulk critical temperature, i.e. at 470 K for n-pentane. Around this temperature, the diffusion coefficient increases by more than one order of magnitude in a temperature range of only about 7 K.

Most importantly, however, around a certain temperature (ca. 438 K for Vycor and ca. 458 for ERM) a remarkable deviation from the Arrhenius pattern in the intrapore diffusivities is observed. We anticipate that this occurs due to transition of the intrapore fluid to the supercritical, more mobile state. It is noteworthy that, in the vicinity of this temperature the diffusivity of the bulk liquid does not show any appreciable deviation from the normal behavior. Importantly, such type of measurements can directly provide the pore critical temperature of fluids introduced into porous solids.

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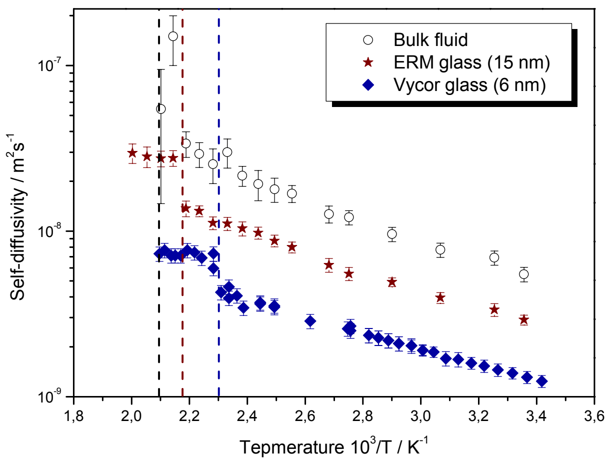

Fig. 1: Arrhenius plot of the bulk (open circles) and pore fluid (solid symbols) diffusivities for *n*-pentane in Vycor porous glass (diamonds) and ERM (stars) as a function of temperature. The vertical dashed lines show the positions of the bulk (black line) and pore critical points for Vycor (brown) and ERM (blue).

References

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[3] R. Valiullin and M. Dvoyashkin, Adsorption-Journal of the International Adsorption Society 13 (2007) 239.