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Supercritical fluids in mesopores—new insight using NMR

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Abstract Supercritical fluids are an essential constitute of modern chemical industry. However, their optimal use in processes involving porous solids is rather limited due to our poor knowledge about their transport properties under confinements. By using the non-invasive pulsed field gradient NMR method, we directly assessed molecular diffusivities of n-pentane in mesopores at sub- and supercritical temperatures. The obtained results ultimately point out that criticality in pores occurs at lower temperatures than in the bulk liquid surrounding the porous solid. The data on molecular diffusivities and pore density may be self-consistently quantified using simple gas-kinetic arguments.

Keywords Supercritical state · Mesopores · Diffusion · NMR

1 Introduction

Supercritical fluids (SCF) exhibit fascinating physico-chemical properties which liquid solvents and gases do not possess, and, thus, are sometimes referred to as phenomenal fluids (Poliakoff and King 2001; Lee et al. 2004). They are highly compressible with liquid-like densities and gas-like transport properties. Small changes in pressure or temperature near the critical point can greatly modify the diffusivity, density and, hence, the solubilizing power of the SCF. Thus, it is possible to tune their physico-chemical properties significantly without changing the molecular structure of a substance especially in the vicinity of the critical point. Being environmentally benign, SCF might be considered and have a wide use as a powerful tool for many chemical applications (DeSimone 2002; Cooper 2003; Baiker 1999; Jessop et al. 1999).

A quite complex situation arises when fluids confined within porous materials are considered. The presence of an additional factor, such as, the interaction with pore walls, may shift the critical conditions and affect the behaviour of SCF notably (Thommes and Findenegg 1994; Burgess et al. 1989; Hiejima and Yao 2004; Gelb et al. 1999).

The critical behavior of fluids under confinements continues to be the subject of a large number of theoretical and experimental studies (Hiejima et al. 2005; Morishige and Shikimi 1998; Arunajatesan et al. 2003; Fretwell et al. 1996; Machin 1999; Brovchenko et al. 2005). One of the hot fields of modern material science concerns the architecture of new types of nanoporous hosts, simultaneously providing chemical multi-functionality and optimized transport properties (Rolison 2003). In the case of extensively used microporous host materials, the latter may be achieved by including void paths of mesoscalic dimensions into the structure, which are supposed to function as fast transport highways for reactant supply and product removal. With respect to these novel materials, SCF may be used as an essential part (i) during fabrication (Cooper 2003) and (ii) as a route to a further improvement of their properties during reaction. As prominent examples to (i), one may refer to the use of supercritical CO_2 to control mesoporous silica (Ghosh et al. 2007; Hanrahan et al. 2005), their subsequent alumination (O'Neil et al. 2002), synthesis of carbon nanotubes in supercritical toluene (Lee et al. 2004). It is quite obvious that even on this stage the detailed knowledge about the behavior of SCF under confinement, namely about their static (phase state)

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and dynamic (transport) properties may become quintessential for the efficient exploration of all their advantages in comparison with conventional solvents. This becomes much more essential on the stage of running chemical processes in porous solids exploiting the very essential features of SCF.

To date, the description of transport properties of SCF under confinement is rather limited to theoretical predictions and some indirect experimental methods, such as, the analysis of sorption-desorption isotherms, performance of catalytic processes in pores and some simulations. Thus, the comprehension of how SCF diffuse in porous solids is still intuitive.

Here, we exploit the pulsed field gradient (PFG) NMR method (Callaghan 1991; Kärger et al. 1988; Kimmich 1997) as a non-invasive method to provide direct quantitative information about diffusion processes of fluids in the bulk (Yoshida et al. 2005) and within porous materials over a broad range of temperatures, including the supercritical region.

2 Materials and method

The diffusion experiments were performed on the NMR spectrometer FEGRIS-400 equipped with a home-built pulsed field gradient NMR probe (Galvosas et al. 2001), operating at a proton resonance frequency of 400 MHz. The high-pressure NMR sample (Fig. 1) allows to measure diffusion coefficients at pressures up to 40 bar and temperatures up to 500 K. These conditions allow to cover both the sub- and supercritical regions of n-pentane that has been used as a probe molecule, with a bulk critical temperature of $T_c \approx 470$ K. Special care has taken to minimize temperature gradients along the sample and associated convection effects (Hedin and Furo 1998; Sorland et al. 2000). In this way, the temperature differences in the sample tube could be kept below 2 K, even at the highest temperatures.

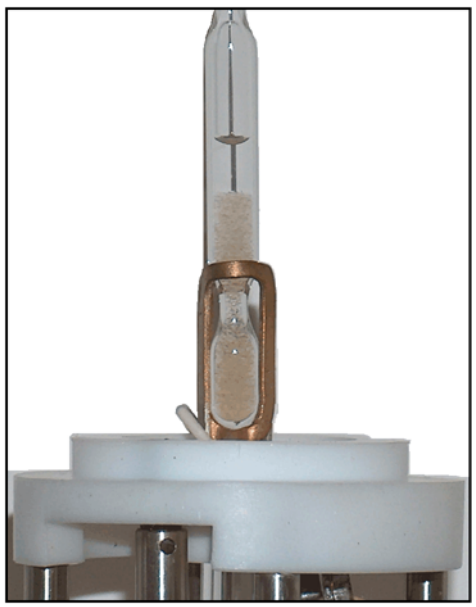

Fig. 1 High-pressure tube with Vycor porous glass and n-pentane in an NMR radio-frequency coil

We have used Vycor porous glass (#7930, 96% SiO_2) (Kikkinides et al. 2000; Levitz et al. 1991) as a mechanically rigid and chemically inert host material of high temperature stability (up to 600 °C). This material is characterized to have highly interconnected mesopores with an average pore diameter of about 6 nm.

The NMR glass tube with crushed Vycor particles of about 500 μm diameter has been filled with an amount of n-pentane providing the critical density $\rho_c = 3.22$ mol/l at the bulk critical temperature. It has been calculated from the total volume of the mesopores and the void space inside the NMR tube. Thus, below the bulk critical temperature the granules of Vycor glass were always surrounded by the liquid.

3 Results and discussion

The self-diffusivities of n-pentane have been directly measured by means of PFG NMR technique in a temperature range of 280–477 K. Figure 2 shows the obtained values as a function of the reciprocal temperature. As a consequence of the biporous structure of the granulated porous glass, two different diffusion coefficients have been extracted. The smaller value reflects diffusion in the mesopores, while the bigger one is referred to the molecules between the granules. This latter diffusivity may be considered to coincide with that of the bulk liquid because, for the diffusion times used in the experiment, the displacements of molecules are much less than the typical distances between granules. These two diffusivities differ by a factor of about five, which is referred to the tortuosity of the Vycor mesopores.

The diffusivities of both the fluid inside the pores and of the bulk phase increase with increasing temperature. In the sub-critical region, they follow the Arrhenius dependence

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right), \tag{1}$$

where D_0 is the pre-exponential factor and E_a the activation energy of diffusion. Applying this fitting procedure, one can see (Fig. 2) that there is no distinct difference in the activation energies between the bulk and intrapore diffusion processes. The values of the activation energies are found to be 10,5 kJ/mol and 9,5 kJ/mol respectively. They are in good agreement with the literature data (Douglass and McCall 1958; Fishman 1955; Dvoyashkin et al. 2007a). The difference is close to the value of experimental uncertainty and, thus, will not be further discussed.

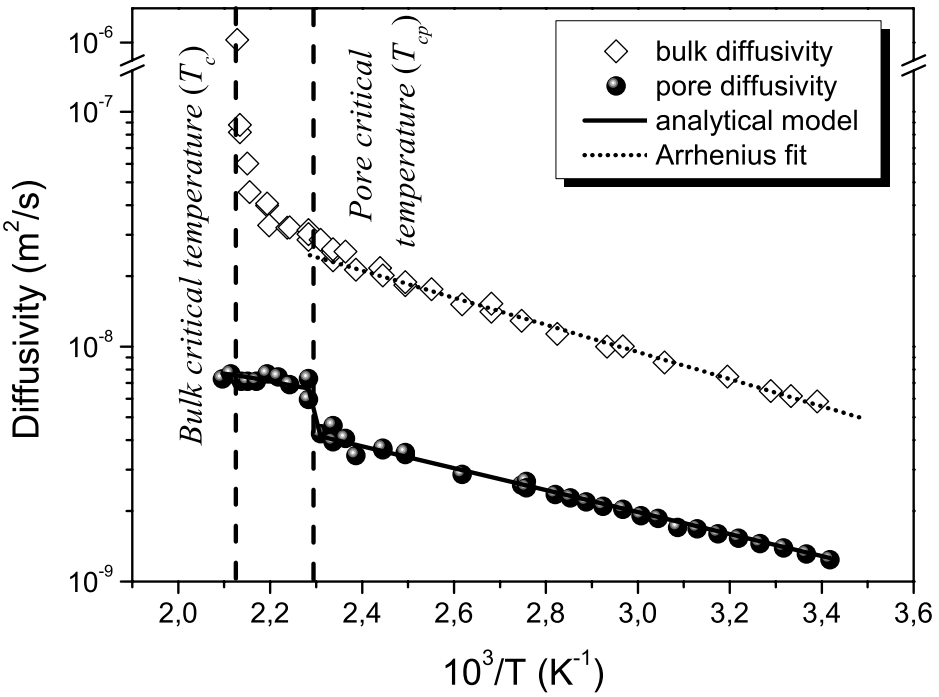

Fig. 2 Arrhenius plot of the bulk and pore fluid diffusivities as a function of temperature. The *solid line* represents the result of the model calculations assuming a transition into the supercritical state at the pore critical temperature $T_{cp} < T_c$. The *vertical dashed lines* show the positions of the bulk (*left line*) and pore (*right line*) critical points. The *dot line* reflects the Arrhenius fit of diffusion data obtained for the bulk component

As expected, for the bulk fluid the transition to the supercritical state takes place at the bulk critical temperature, i.e. at $T_c \approx 470$ K. Such a transition is identified in the critical region, where a dramatic deviation from the Arrhenius behavior could is observed. The diffusion coefficient increases by more than one order of magnitude in a temperature range of only about 7 K.

In contrast to this, for the pore fluid this sharp jump in the diffusivities is already observed at a temperature of about 30 K below the bulk critical temperature (Dvoyashkin et al. 2007b). Interestingly, with further increasing temperature up to 477 K increase in the diffusivities is much smaller than in the bulk case. The formation of such a plateau may be rationalized by realizing that now molecular propagation is essentially restricted by Knudsen diffusion which, in turn, is controlled by the pore size (about 6 nm).

For a quantitative estimate of the diffusivity above the pore critical temperature T_{cp}, we introduce the mean density $\bar{\rho}_p$ in the pores. It may be represented as

$$\bar{\rho}_p = f_a \rho_a + f_i \rho_i, \tag{2}$$

where f_a and f_i are the fractions ($f_a + f_i = 1$) of molecules at the pore walls and in the pore interior with the corresponding densities ρ_a and ρ_i, respectively. f_a is taken to correspond to one monomolecular layer at the pore walls having the density of bulk state. ρ_i is taken to be equal to the supercritical density. Since, over molecular displacements of micrometers as considered in our experiments, there is fast exchange between these two phases, the effective diffusivities D in the pores obey the relation:

$$D = f_a D_a + f_i D_i, \tag{3}$$

where D_a and D_i are the diffusivities in the adsorbed phase and of the fluid in the pore interior, respectively. As a crude estimate, we can take D_a to behave as the intrapore diffusivity at full pore saturations, i.e. model it by the Arrhenius law using the data at $T < T_{cp}$. D_i is calculated using the gas-kinetic approach

$$\frac{1}{D_i} = \frac{1}{D_M} + \frac{1}{D_K}. \tag{4}$$

Here, D_M and D_K are the molecular and the Knudsen diffusivities given, respectively, by $D_M = \lambda\bar{\vartheta}/3$ and $D_M = d\bar{\vartheta}/3$, where $\bar{\vartheta}$ is the mean molecular velocity, λ is the mean free path of the bulk fluid, and d is the pore diameter. The resulting curve is given as the solid line in Fig. 2 and is in perfect agreement with the experimental data. It has to be pointed out, that the analytical model is free from any fitting parameters. It is a result of direct calculations!

4 Conclusions

Measuring self-diffusion coefficients by means of PFG NMR provides a direct way to follow dynamical characteristics of molecules confined to nanoporous materials as well as in the bulk phase. This study represents direct measurements of the transport properties of the n-pentane molecules confined to the mesopores of Vycor porous glass and,

simultaneously, of the bulk liquid surrounding the porous solid up to supercritical conditions. The critical point of the confined fluid was reached at a temperature of about 30 K below that of the bulk which, at this temperature, was still present as two phases, namely as a gas and a liquid. In the vicinity of the pore critical point the diffusivity of the confined fluid increases by a factor, predominantly determined by the pore size. Following the Knudsen mechanism, the diffusivity remains essentially constant with further increasing temperature. The options to tune the fluid properties, and hence their performance in chemical application, are thus shown to be relevant also for mass transfer within mesoporous solids, although not as pronounced as in bulk fluids. Thus, it may provide a basis for a rational use of SCF within porous solids in applications such as extraction, adsorption, or heterogeneous catalysis.

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