

DIFFUSION OF SUPERCRITICAL FLUIDS IN MESOPOROUS MATERIALS STUDIED BY PFG NMR

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Abstract. Supercritical fluids (SCF) offer attractive opportunities for modern chemical industry. Their optimal use in processes involving porous solids requires a better understanding of their behavior under confinement. In particular, there is not much known about the transport properties of SCFs in small pores, which is primarily determined by an almost complete lack of relevant experimental studies. In this contribution we show that nuclear magnetic resonance (NMR) provides a powerful set of tools (methods) to cover various aspects of the problem. Thus, the pulsed field gradient NMR method yields data on molecular self-diffusivities of SCF in mesopores – the information which has not directly been assessed before. The temperature dependencies of the measured diffusivities point out that the transition to the supercritical state in pores occurs far in advance to that of the bulk fluid. We anticipate that the analysis of the data on transport properties and the data on the fluid density, accessible using different NMR methods, may provide a comprehensive picture on the state and properties of SCFs in porous solids and provide important experimental data for applied sciences, especially for chemical engineering.

Keywords: supercritical state, mesopores, diffusion, NMR

INTRODUCTION

Supercritical fluids represent a unique class of substances with physical properties typical for both liquids and gases [1]. 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 [2], [3]. Importantly, SCF such as supercritical water or carbon dioxide have the potential to replace previously used toxic and environmentally dangerous solvents, making a step forward approaching green chemistry [4]. In parallel to the environmental aspects, use of SCF in such processes, e.g. 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. The main objective of this work is the elucidation of the physical properties of SCF under confinement by means of NMR methods, especially the pulsed field gradient (PFG) NMR technique providing unique options for this purpose[5][6, 7][5-7].

Phase behavior of fluids in pores at near- and supercritical conditions has been the subject of numerous studies [8][9][10][8-10]. The overwhelming part of these is focused on the fluid densities and their anomalies with varying temperature or pressure under the conditions of confinement inside pores of solid materials.

Transport properties, which are essential not only for reaction operation [11] but also for the understanding of the very nature of their intrinsic dynamics, were, so far, accessed indirectly by model-based analysis of diffusion-related processes (like catalytic conversions) [12] or by theoretical calculations [13]. One of the simple ways to assess the effective diffusivity is based on measuring sorption kinetics. Thereafter, to evaluate the diffusivity, a certain model has to be used which has to account for many complex phenomena occurring and, therefore, affecting the sorption behavior [14].

Astonishingly, although there exists a great demand for experimental data, experimental methods providing direct information about molecular transport such as PFG

NMR or light-scattering methods have so far not been applied to confined SCFs. At the same time, NMR, being a powerful and, importantly, a non-invasive technique, has already been exploited to follow several processes under supercritical conditions. Yonker and Linehan [15] provide an extensive review on this topic with many relevant examples. Moreover, the application of the PFG NMR method to supercritical water, providing accurate measurements of the self-diffusion constants of water at near- and supercritical conditions, has been recently reported [16]. Owing to these studies demonstrating the possibility to run and operate NMR under supercritical conditions requiring high temperatures and pressures, it seems to be very promising to extend this type of measurements to confined near- and supercritical fluids [17]. The success of such an extension seems to be realistic in view of the high technical level of modern NMR instrumentation and the advanced methodology of NMR techniques for studying transport processes of fluids in porous materials.

The main purpose of the present work is the direct assessment of transport properties of fluids confined to mesopores at high temperatures and pressures including supercritical conditions.

MATERIALS AND METHODS

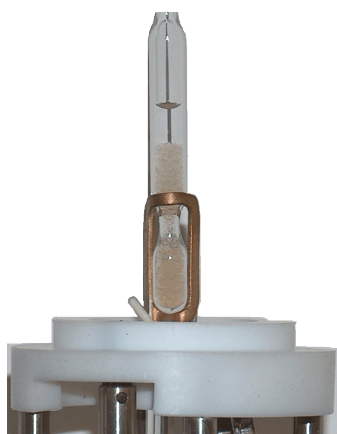


Figure 1. High-pressure tube with Vycor porous glass and n-pentane in an NMR radio-frequency coil.

The NMR glass tube (Fig. 1) with crushed Vycor porous glass [18] particles of about 500 μm size having internal mesoporous structure with a mean pore diameter of about 6 nm has been filled under vacuum with such an amount of n-pentane to yield the critical density $\rho_c = 3.22 \text{ mol/l}$ at the bulk critical temperature $T_c \approx 470 \text{ K}$. In order to calculate the required amount of the liquid, both the free volume between the particles in the tube and the volume of the mesopores have been considered. The found amount was sufficient to completely cover the Vycor particles, i.e. during the experiments they were always surrounded by the liquid phase at temperatures below T_c . At these temperatures, a well-defined meniscus dividing the vapour and the liquid phases is observed.

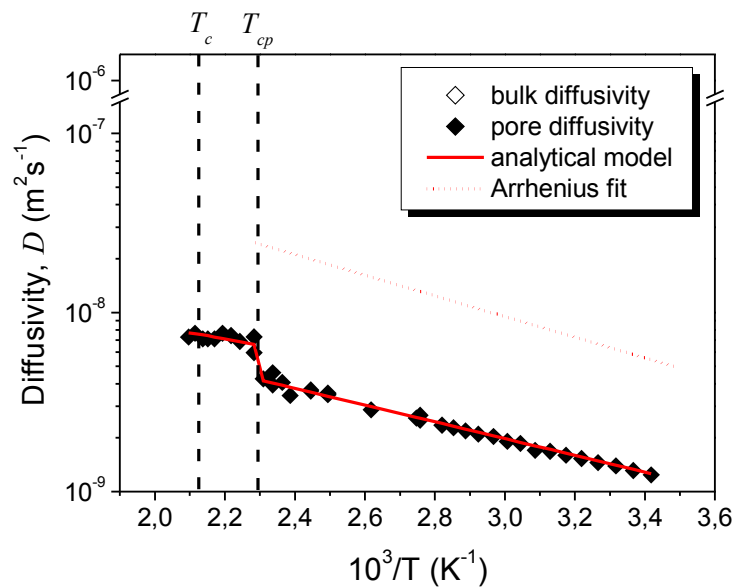
The diffusion experiments were performed on the NMR spectrometer FEGRIS-400 equipped with a home-built pulsed field gradient NMR probe [19], operating at a proton resonance frequency of 400 MHz. The high-pressure NMR sample allows to measure diffusion coefficients at a working pressure up to 40 bar and temperatures up to 500 K. These conditions allow to cover both the sub- and supercritical regions of n-pentane. Special care was taken to minimize temperature gradients along the sample and associated convection effects. In this way, the temperature differences in the sample tube could be kept below 2 K, even at the highest temperatures.

RESULTS

Diffusion experiments.

The self-diffusivities of n-pentane have been directly measured by means of the PFG NMR technique in a temperature range of 280–477 K. Fig. 2 shows the obtained values as a function of the reciprocal temperature. As a consequence of the bimodal pore system of the granulated porous glass, two different diffusion coefficients have been extracted. The smaller value reflects diffusion in the mesopores, while the larger refers 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 five, which is referred to the tortuosity of the Vycor mesopores.

Figure 2. Arrhenius plot of the bulk and the pore fluid diffusivities as a function of temperature. The solid line represents the result of model calculations assuming a transition to 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 dotted line reflects the Arrhenius fit of diffusion data obtained for the bulk component.



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

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

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 [20, 21][20, 21]. The difference is close to the value of experimental uncertainty and, thus, will not be further discussed.

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 is observed. The diffusion coefficient increases by more than one order of magnitude in a temperature range of only about 7 K.

In contrast, for the pore fluid this sharp jump in the diffusivities is already observed at a temperature 30 K below the bulk critical temperature. Interestingly, with further increasing temperature up to 477 K the rise 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 [22] 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 fluid density $\bar{\rho}_p$ in the pores. It may be represented as

$$\bar{\rho}_p = f_a \rho_a + f_i \rho_i \quad (2)$$

where f_a and f_i are the fractions ($f_a + f_i = 1$) of molecules adjacent to 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 [5]:

$$D = f_a D_a + f_i D_i \quad (3)$$

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

$$\frac{1}{D_i} = \frac{1}{D_M} + \frac{1}{D_K} \quad (4)$$

Here, D_M and D_K are the molecular and the Knudsen diffusivities given, respectively, by $D_M = \lambda \bar{v} / 3$ and $D_K = d \bar{v} / 3$, where \bar{v} is the mean molecular velocity, λ is the mean free path of the bulk fluid, and d is the pore diameter. The resulting curve (note that no fitting parameters have been used) is given as the solid line in Fig. 2 and is in perfect agreement with the experimental data.

Visual experiments.

Under supercritical conditions density of a fluid becomes supercritical, that is $\rho_c = 3.22$ mol/l for n-pentane. If, as mentioned above, supercriticality inside pores might appear at lower temperature as compared to bulk, the density alteration of a fluid inside pores must have an influence on the behavior of the meniscus between excess bulk liquid surrounding glass particles and its saturated vapor phase. Fig. 3 shows three snapshots of the sample tube at room $T_{room} = 298$ K, pore critical $T_{cp} = 438$ K and bulk critical $T_c = 470$ K temperatures. Starting from room temperatures the heating of the sample tube is accompanied by the enhancement of the meniscus level until its complete disappearance at the bulk critical temperature (Fig. 3, c). With a temperature step of 1 K and equilibration time of 20 minutes for each temperature value the negative influence of convection effects has been minimized.

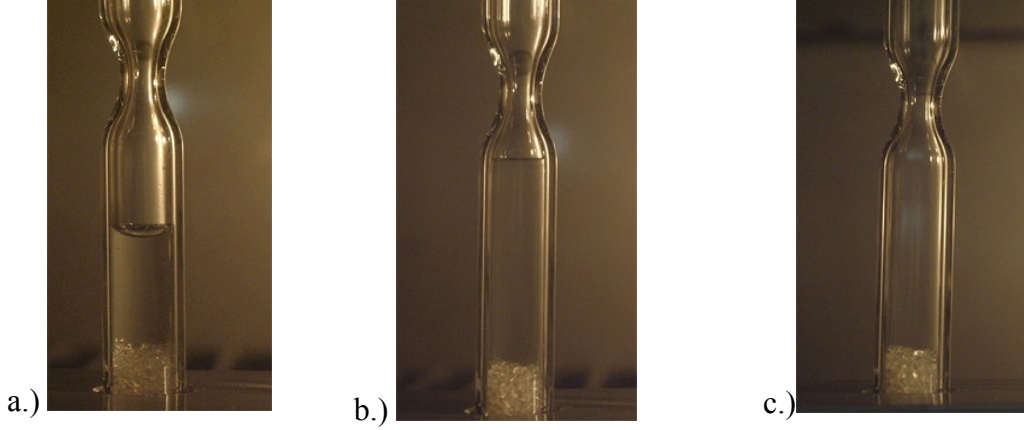
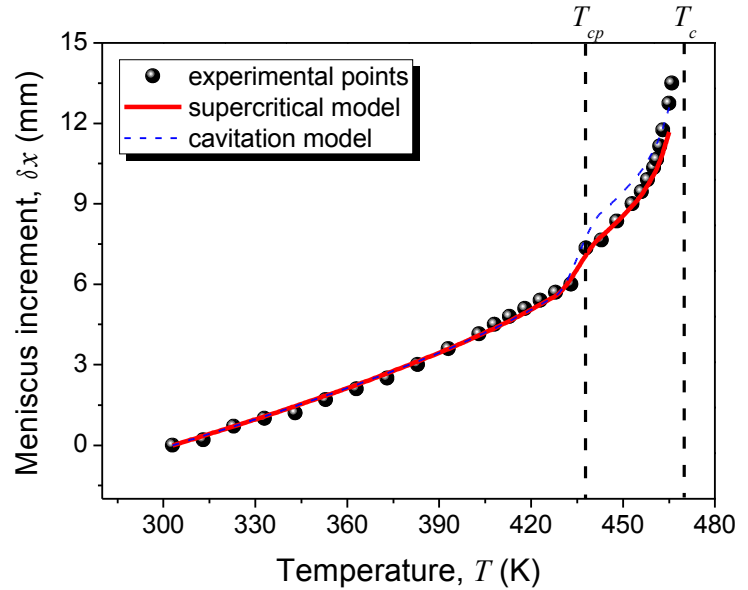


Figure 3. Photographs demonstrating the location of the meniscus at a.) room temperature, b.) pore critical temperature and c.) its disappearance as the critical point for the pure substance-pentane is reached.

The variation of the meniscus level δx upon changing temperature, driven by the change of the fluid densities, is shown in fig. 4. Interestingly, at temperatures close to the pore critical temperature $T_{cp} = 438$ K, estimated from diffusion experiment, a discontinuous change of δx has been observed. With the known density dependence of the bulk phase and the pore size and porosity of Vycor, the position of the meniscus upon temperature variation may be rationalized using simple gas-kinetic arguments by following models. Two possible scenarios which may explain the observed behavior have been considered: (i) transition to the supercritical state and (ii) nucleation of gas bubbles in the pores, that is cavitation.

Figure 4. Variation of the meniscus level δx with respect to the meniscus position at 298 K with changing temperature. The broken line shows the meniscus level calculated under the assumption of no transition to the supercritical state. The solid line is obtained assuming that the fluid in the pore interior attains the supercritical density at $T = T_{cp} < T_c$.



The total number of molecules Z_0 inside tube distributed between liquid and vapour phase with corresponding densities $\rho_l(T)$, $\rho_g(T)$:

$$\rho_l V_l + \rho_g V_g = Z_0 \quad (5)$$

where $V_l(T)$, $V_g(T)$ - volumes occupied by molecules of liquid phase in the bulk as well as in the pore interiors and vapour phase, respectively. Taking into account the known amount of n-pentane inside tube and geometrical parameters of a sample tube, one can figure out the expression describing temperature dependence of a meniscus level in a sealed tube in the subcritical region (below T_{cp}):

$$\delta x_{subcritical}(T) = \frac{1}{\pi R^2} \left\{ \frac{\frac{Z_0}{\rho_g(T)} - V_0}{\frac{\rho_l(T)}{\rho_g(T)} - 1} - V_{l|T=298K} \right\} \quad (6)$$

Here $\delta x_{subcritical}$ is the temperature dependent meniscus increment, R is the radius of the glass tube and $V_{l|T=298K}$ is the volume of a liquid at room temperature.

Above the pore critical point T_{cp} the existence of supercritical phase inside pores (or gaseous phase in case of cavitation) leads to appearance in eq. (5) of a third term $\bar{\rho}_p V_p$ responsible for intrapore component (see eq. (2)):

$$\rho_l V_l + \rho_g V_g + \bar{\rho}_p V_p = Z_0 \quad (7)$$

where V_p is the total pore volume. Taking into account the presence of a liquid-like monolayer adsorbed on the surface of pore walls, even under supercritical conditions, and assuming the cylindrical shape of pores of Vycor porous glass, the average density inside pores is performed as following

$$\bar{\rho}_p = 0.5\rho_l + 0.5\rho^* \quad (8)$$

where ρ^* is the density of the critical (or gaseous, in case of cavitation) phase inside pores. Finally, the meniscus increment in critical region is performed by

$$\delta x_{critical} = \frac{1}{\pi R^2} \left(\frac{Z_0 - V_0 \rho^*}{\rho_l - \rho^*} + \frac{1}{2} V_p - V_{l|T=298K} \right) \quad (9)$$

Thus, the appearance of gas bubbles should correspond to model where $\rho^* = \rho_g$, while the case $\rho^* = \rho_{cr}$ implies the existence of the supercriticality. Fig. 4 shows that supercritical model perfectly follows the experimental data points while the cavitation model significantly deviates in range of temperatures close to the pore critical temperature. Thus, the combined analysis unequivocally pointed out that only the supercritical model self-consistently describes the overall behavior of the fluid observed in the experiments.

CONCLUSION

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. The pore diffusivities and densities of a mesopore-confined fluid in both the subcritical and supercritical states have been correlated on the basis of straightforward model arguments. This helps, in particular, to rationalize that around the bulk critical temperature, i.e. in the range of the dramatic increase in the bulk diffusivities, pore diffusion could already proceed in the supercritical state. At higher temperatures, the diffusivity in the mesopore remains essentially constant being determined by the mean free path in the pore space according to the Knudsen limit of diffusion. We consider this experimental study as a key experiment showing that such type of measurements and subsequent analysis will certainly provide deep insight into the physics of critical fluids under mesoscale confinement.

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REFERENCES:

- [1] M. Poliakoff and P. King, *Nature* 412 (2001), p. 125.
- [2] A. Baiker, *Chemical Reviews* 99 (1999), p. 453.
- [3] P. G. Jessop, T. Ikariya and R. Noyori, *Chemical Reviews* 99 (1999), p. 475.
- [4] J. M. DeSimone, *Science* 297 (2002), p. 799.
- [5] J. Kärger, H. Pfeifer and W. Heink, *Advances in Magnetic Resonance* 12 (1988), p. 2.
- [6] W. S. Price, *Concepts in Magnetic Resonance* 9 (1997), p. 299.
- [7] W. S. Price, *Concepts in Magnetic Resonance* 10 (1998), p. 197.
- [8] C. G. V. Burgess, D. H. Everett and S. Nuttall, *Pure and Applied Chemistry* 61 (1989), p. 1845.
- [9] W. D. Machin, *Langmuir* 15 (1999), p. 169.
- [10] M. Thommes and G. H. Findenegg, *Langmuir* 10 (1994), p. 4270.
- [11] D. R. Rolison, *Science* 299 (2003), p. 1698.
- [12] V. Arunajatesan, K. A. Wilson and B. Subramaniam, *Industrial & Engineering Chemistry Research* 42 (2003), p. 2639.
- [13] J. Zhou and W. C. Wang, *Langmuir* 16 (2000), p. 8063.
- [14] T. Dogu, *Industrial & Engineering Chemistry Research* 37 (1998), p. 2158.
- [15] C. R. Yonker and J. C. Linehan, *Progress in NMR Spectroscopy* 47 (2005), p. 95.
- [16] K. Yoshida, C. Wakai, N. Matubayasi, M. Nakahara, *Journal of Chemical Physics* 123 (2005).
- [17] M. Dvoyashkin, R. Valiullin, J. Karger, W. D. Einicke and R. Glaser, *Journal of the American Chemical Society* 129 (2007), p. 10344.
- [18] T. H. Elmer, *Engineered Materials Handbook*, ASM (1992).
- [19] P. Galvosas, F. Stallmach, G. Seiffert, J. Karger, U. Kaess and G. Majer, *Journal of Magnetic Resonance* 151 (2001), p. 260.
- [20] D. C. Douglass and D. W. McCall, *Journal of Physical Chemistry* 62 (1958), p. 1102.
- [21] M. Dvoyashkin, R. Valiullin and J. Karger, *Physical Review E* 75 (2007).
- [22] W. G. Pollard and R. D. Present, *Physical Review* 73 (1948), p. 762.
- [1] M. Poliakoff, and P. King, *Nature* 412, 125 (2001).
- [2] A. Baiker, *Chemical Reviews* 99, 453 (1999).
- [3] P. G. Jessop, T. Ikariya, and R. Noyori, *Chemical Reviews* 99, 475 (1999).
- [4] J. M. DeSimone, *Science* 297, 799 (2002).
- [5] J. Kärger, H. Pfeifer, and W. Heink, *Advances in Magnetic Resonance* 12, 2 (1988).
- [6] W. S. Price, *Concepts in Magnetic Resonance* 10, 197 (1998).
- [7] W. S. Price, *Concepts in Magnetic Resonance* 9, 299 (1997).
- [8] C. G. V. Burgess, D. H. Everett, and S. Nuttall, *Pure and Applied Chemistry* 61, 1845 (1989).
- [9] M. Thommes, and G. H. Findenegg, *Langmuir* 10, 4270 (1994).
- [10] W. D. Machin, *Langmuir* 15, 169 (1999).
- [11] D. R. Rolison, *Science* 299, 1698 (2003).
- [12] V. Arunajatesan, K. A. Wilson, and B. Subramaniam, *Industrial & Engineering Chemistry Research* 42, 2639 (2003).
- [13] J. Zhou, and W. C. Wang, *Langmuir* 16, 8063 (2000).
- [14] T. Dogu, *Industrial & Engineering Chemistry Research* 37, 2158 (1998).
- [15] C. R. Yonker, and J. C. Linehan, *Progress in Nuclear Magnetic Resonance Spectroscopy* 47, 95 (2005).
- [16] K. Yoshida et al., *Journal of Chemical Physics* 123 (2005).
- [17] M. Dvoyashkin et al., *Journal of the American Chemical Society* 129, 10344 (2007).
- [18] T. H. Elmer, in *Engineered Materials Handbook* (ASM, 1992), pp. 427.
- [19] P. Galvosas et al., *Journal of Magnetic Resonance* 151, 260 (2001).
- [20] D. C. Douglass, and D. W. McCall, *Journal of Physical Chemistry* 62, 1102 (1958).
- [21] M. Dvoyashkin, R. Valiullin, and J. Karger, *Physical Review E* 75 (2007).

[22] W. G. Pollard, and R. D. Present, *Physical Review* 73, 762 (1948).