

Diffusion and phase equilibria of binary fluids in mesopores

Philipp Zeigermann · Muslim Dvoyashkin ·
Rustem Valiullin

Received: 14 May 2010 / Accepted: 28 October 2010 / Published online: 6 November 2010
© Springer Science+Business Media, LLC 2010

Abstract The formation of adsorption hysteresis in mesoporous material with random pore structure may be interrelated with different distributions of the fluid density attained along different paths of the system preparation. To access microscopic details of these distributions, in addition to the main sorptive liquid, distribution of which along the pore space of Vycor porous glass was of interest, a small amount of a probe liquid with a substantially lower vapor pressure has been added. Molecular diffusivities of both liquids then have been traced using pulsed field gradient NMR. Due to different vapor pressures, the two molecular species explore different spaces occupied by the capillary-condensed (accessible for both species) and gaseous (accessible only for the molecules of the main sorptive) phases. Comparative analysis of the diffusion properties obtained at different states along the adsorption isotherm revealed further insight into peculiarities of the fluid distribution and mass transfer of binary fluids in pores.

Keywords Adsorption · Diffusion · Binary mixture · Mesoporous materials · Nuclear magnetic resonance

1 Introduction

Permanent interest to mesoporous host materials is, in particular, determined by their better transport properties as compared to widely used microporous adsorbents. As to one of the specific consequences of the mesoscalic pore

dimension, one may refer to occurrence of the capillary-condensation and evaporation transitions at the gas pressures well below the bulk equilibrium transition pressure. In addition, in mesopores these two transitions typically exhibit hysteresis phenomena, i.e., they occur at distinct pressures. A particular shape of the adsorption hysteresis loop is determined by the structural properties, such as pore size distribution and pore space morphology. In materials with random pore structures, it has been anticipated that hysteresis may be interrelated with different distributions of the fluid within the pore matrix along the adsorption and desorption branches. This may be a result of an interplay of different mechanisms contributing to the hysteresis formation, such as pore blocking and metastability effects on a single-pore level. From the experimental point of view, while the average behavior, e.g. sorption isotherms, can easily be measured by a variety of experimental techniques, the microscopic topological distribution of the fluid density in the pore matrices is much more difficult to access (Page et al. 1995; Jähnert et al. 2009).

Recently, it has been shown that nuclear magnetic resonance (NMR) may grant deeper insight into this problem by assessing molecular diffusivities along with sorption behavior (Naumov et al. 2008). In particular, it was found that, depending on the history how a given state is attained, diffusivities of the fluid in these states may differ. Although qualitative hypotheses to explain the behavior obtained was provided, a more quantitative analysis was prohibited due to the complex mass transfer mechanism including a combination of diffusion in the capillary-condensed and gaseous phases. In this work, we went further in this direction by considering binary liquids where one of the components was used to probe spatial arrangement of the second mixture component within the pore matrix. The idea was to suppress one of the diffusion pathways for one of the liquid components, namely

P. Zeigermann · M. Dvoyashkin · R. Valiullin (✉)
Department of Interface Physics, University of Leipzig,
Linnéstr. 5, 04103 Leipzig, Germany
e-mail: valiullin@uni-leipzig.de

transport through the gaseous phase in pores. Therefore, as the probe species we have used a small amount (to not impact phase equilibria of the main sorptive) of relatively large molecules with a low vapor pressure (to suppress diffusion through the gaseous phase). Thus, one may expect that if one and the same amount of liquid is differently distributed along the pores, the probe molecules should have different diffusivities due to different tortuosities experienced by them in unlike environments. In this way, we have expected that a comparative analysis of the diffusion properties of the binary liquid components may provide additional information about fluid configuration in the pores.

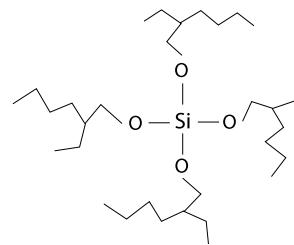
Besides pure fundamental interest concerning the formation of adsorption hysteresis and all its accompanying phenomena, access to transport properties of multi-component fluids confined to small pores is itself of technological importance. This type of systems is often found in, e.g., polymer electrolyte fuel cells (Pasaogullari and Wang 2004). That is why diffusion of liquid mixtures in mesoporous matrices at full pore saturations has already been widely addressed, especially in the context of microphase separation (Valiullin and Furo 2002; Hellweg et al. 2003). Similar studies under conditions of porous materials only partially saturated by liquids, however, mostly dealt with multicomponent surface diffusion in relation with adsorption equilibrium (Tuchlenski et al. 1998; Valiullin et al. 2005). Thus, the second objective of this work was to experimentally study the transport properties of binary liquids in mesopores at partial pore fillings.

2 Materials and methods

As a model mesoporous material, Vycor porous glass (7930) has been used (Wiltzius et al. 1987; Levitz et al. 1991; Kainourgiakis et al. 1999). This material possesses a random pore structure with a relatively narrow distribution of pore diameters centered around about 5 nm and having a porosity of 28%. Importantly, this material is available in a monolithic form. In our study, we have used a rod of Vycor porous glass with a diameter of 6 mm and a height of 1 cm. Before the use, it was cleaned according to a recipe provided by the manufacturer (Elmer 1992).

After cleaning, Vycor porous glass was placed in an NMR glass tube and the pore space has been saturated by the binary liquid under study. The choice of the test liquid components has been defined by the goals of this study. According to them, one of the liquid components, namely cyclohexane, was chosen to have good affinity to the pore walls and to possess sufficiently high vapor pressure. The latter allowed to have better control over the pore saturation via the gas pressure. The second component, in opposite, was chosen to have sufficiently low vapor pressure and no specific interactions with the pore

Fig. 1 Chemical structure of tetrakis(2-ethylhexoxy)silane (TEHOS)



walls and cyclohexane. As a good candidate, we found tetrakis(2-ethylhexoxy)silane (TEHOS), the chemical structure of which is shown in Fig. 1. TEHOS and cyclohexane were purchased from ABCR GmbH (Germany) and Sigma-Aldrich (Germany), respectively, and were used without further purification.

The binary liquid consisting of 2 mol percents of TEHOS, and 98 mol percents of cyclohexane was prepared by mixing the two components. After full saturation of the Vycor porous glass monolith with the mixture under vacuum, the sample was connected to a big reservoir containing cyclohexane vapor at a pressure just slightly below its saturation pressure. During further desorption, by reducing the cyclohexane vapor pressure in the reservoir, cyclohexane is preferably evaporated due to its high vapor pressure. TEHOS, as a liquid having much lower vapor pressure, resides in the pores.

Self-diffusivities of cyclohexane and TEHOS were measured using a home-built NMR spectrometer operating at 400 MHz ^1H resonance frequency and equipped with a pulsed field gradient unit (Galvosas et al. 2001). For the diffusion measurements, the 13-interval pulse sequence (Cotts et al. 1989) was used. Measurements have been performed with the use of different diffusion times t from 6 ms to 1 s. The ^1H spin-echo signal measured is, in our case, contributed by protons belonging to two different mixture components with different molecular mobilities. Therefore, the diffusion attenuations $A(q^2, t)$ ($q \equiv \gamma \delta g$ is the wave number controlled in the experiments, γ is the gyromagnetic ratio, δ and g are the duration and the intensity of the magnetic field gradient pulses) were obtained being of non-exponential form, as shown by Fig. 2. The normalized functions $S_n \equiv A(q^2, t)/A(0, t)$ were satisfactorily approached by the weighted sum of two exponential functions:

$$S_n = p_T \exp\{-q^2 t D_T\} + p_C \exp\{-q^2 t D_C\}, \quad (1)$$

where D_T and D_C are the diffusivities of TEHOS and cyclohexane, respectively. The relative weights p_T and p_C ($p_T + p_C = 1$) of the two liquids in the normalized diffusion attenuations S_n are related to the relative proton fractions of the two liquids in the mixture. Due to different nuclear transverse relaxation rates, p_T and p_C appear to be relaxation-weighted and, therefore, should be treated with care.

To control the pore filling in the Vycor porous glass, the ^1H free induction decay signal intensity was used (Valiullin

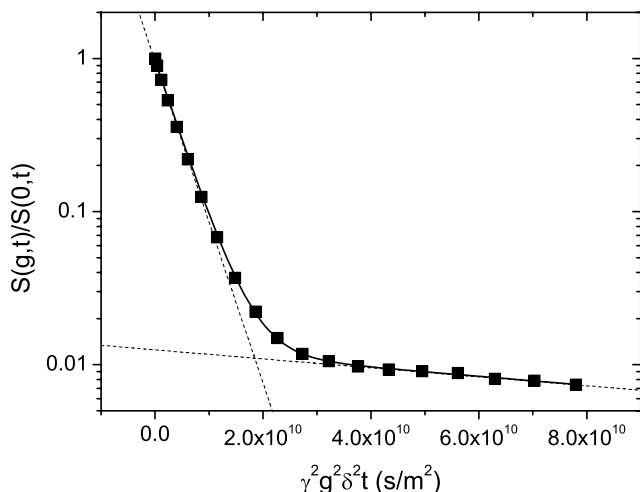


Fig. 2 Typical ^1H spin-echo diffusion attenuation function S_n for cyclohexane-TEHOS mixture in Vycor porous glass at full pore loading. The solid line shows best fit of (1) to the experimental data. The resulting components are shown by the dotted lines

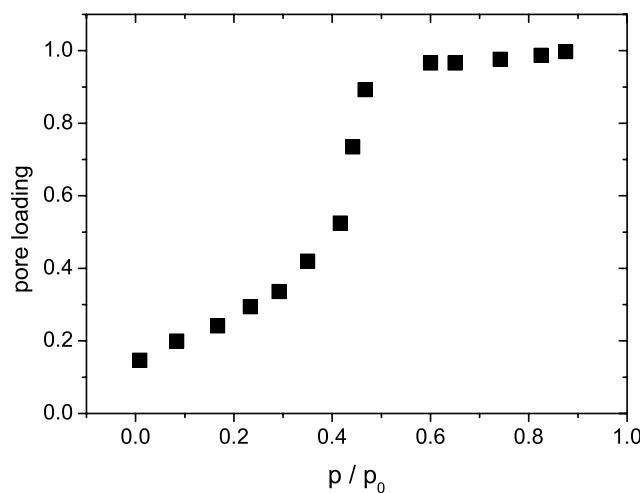


Fig. 3 The overall pore loading by the cyclohexane-TEHOS mixture as a function of the relative cyclohexane gas pressure p/p_0 as measured by NMR on desorption

et al. 2004). It is directly proportional to the overall number of ^1H nuclei in the sample. To calibrate the signal, it was assumed that at zero gas pressure only TEHOS remains in the pores, while at the pressures close to the saturated vapor pressure of cyclohexane, the latter occupies 90% of the pore volume (90% is cyclohexane volume fraction in the bulk binary mixture). The thus measured, normalized quantity is shown in Fig. 3 and is referred to as pore loading.

3 Experimental results and discussion

As it was discussed in the preceding section, the diffusion spin-echo attenuations S_n measured at different exter-

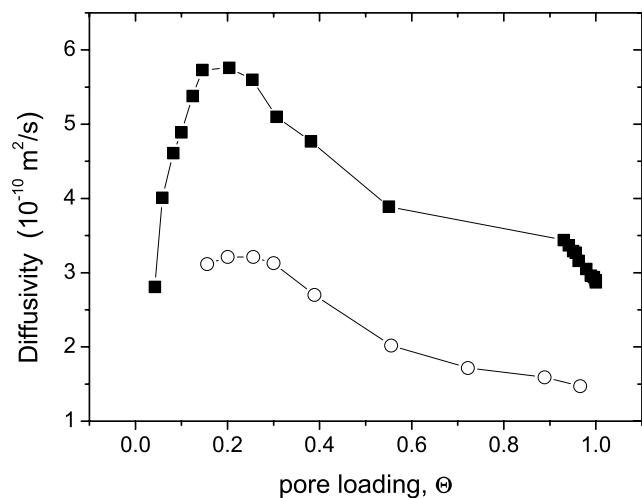


Fig. 4 Diffusivities of cyclohexane as a function of the overall pore loading for pure cyclohexane (filled symbols) and cyclohexane-TEHOS mixture (open symbols) as observed by PFG NMR upon desorption

nal conditions, corresponding to different loadings θ of cyclohexane in the pores, have been satisfactorily fitted to (1). This is exemplified by Fig. 2. Note that the use of a bi-exponential function to approach the experimental data is, in our case, justified referring to the fact that the two molecules used (cyclohexane and TEHOS) have of about two-fold difference in their hydrodynamic radii. This, consequently, leads to about two orders of magnitude difference in their respective self-diffusivities. As a result, these liquids are easily distinguishable in the spin-echo diffusion attenuation functions.

On the other hand, the bi-exponential character of S_n tells that the diffusivities of both cyclohexane and TEHOS do not show any appreciable distributions (due to, e.g., microphase separation). Otherwise, it would lead to a more complex shape of S_n as compared to (1). Thus, on the length scale above that probed by the molecules during the observation times t , there should be no observable differences in the distribution of the binary liquid. In what follows, we present the results obtained using this fitting procedure.

Figure 4 shows diffusivities of cyclohexane as a function of pore loading attained on the desorption branch. For comparison, the data obtained with pure cyclohexane are also shown (Valiullin et al. 2006). The formation of the maximum in the diffusivities for pure liquids has already been thoroughly discussed in the literature Valiullin et al. (2004, 2006). Here we only recall the main mechanisms contributing to this behavior. Starting from full loading of the mesopores, the density of the intrapore liquid first slightly decreases with decreasing gas pressure. The thus obtained stretched liquid exhibit higher diffusivities. Upon attaining a certain pressure, evaporation transition does occur as evidenced by the sharp decrease of the pore loading at $p/p_0 \approx 0.4$ in Fig. 3. As a consequence, the effective diffusivity in-

creases further due to cyclohexane molecules in the gaseous phase. They enhance the overall mass transfer due to higher diffusivities in the gaseous phase. Further desorption in the regime of no capillary-condensed phase in the pores, leads to decrease of the gas density, therefore diminishing the contribution of the gas phase to the overall mass transfer.

In the presence of TEHOS, the diffusion behavior of cyclohexane D_C changes both quantitatively and qualitatively. Here we would like to point out a few differences. (i) At full loading of the mesopores by the binary liquid, the absolute value of D_C drops down by a factor of about two, as compared to the case of pure cyclohexane. This is presumably caused by a hindering effect by the introduced TEHOS molecules. (ii) Interestingly, in the initial stage of desorption the steep increase in the diffusivities of pure cyclohexane (referred to a stretching in the capillary-condensed phase) is not observed in the mixture. This observation may reveal that the formation of the menisci, resisting to the gas invasion into the pores at the pore necks, is prohibited due to TEHOS. Whether it is driven by, e.g., a decrease of the cyclohexane-pore wall interaction due to preferential adsorption of TEHOS by the pore walls or due to some impact of TEHOS on the liquid-gas interface properties could not be concluded from our experiments. (iii) No strong decrease of cyclohexane diffusivities with decreasing loading in the region from multi-layer to sub-monolayer adsorption is observed. This may presumably be related to the fact that the surface sites (or locations) with higher adsorption energies are preferentially occupied by TEHOS molecules. Therefore, with preadsorbed TEHOS molecules, the surface appears to be energetically more homogeneous for cyclohexane, as compared to the case of adsorption of pure cyclohexane. Similar effect has already been reported for surface diffusion of cyclohexane-nitrobenzene mixture in siliceous materials (Valiullin et al. 2005). Indeed, according to a diffusion model, taking account of equilibrium between adsorbed and gaseous phases in pores, stronger dependence of the diffusivities on surface coverage is expected for more heterogeneous surfaces in this regime (Valiullin et al. 2004).

For TEHOS, upon varying the pore loading, a totally different behavior is observed. Figure 5 shows that in the region of pore loadings from about 0.1 (no cyclohexane in the pores, the loading is determined only by TEHOS) to about 0.5 the diffusivity of TEHOS does not change within the experimental uncertainty. Upon further saturation, the diffusivity increases, in contrast to cyclohexane. The former fact is attributed to a predominant effect of surface interaction for TEHOS molecules at these loadings. Note that, assuming cylindrical pore geometry and a pore diameter of about 6 nm, $\theta = 0.5$ corresponds to a liquid film of a thickness of about 1 nm covering the pore walls and that for $\theta < 0.5$ there scarcely exist extended regions containing the capillary-condensed liquid. Thus, due to a film thickness similar to the diameter of TEHOS molecules, the latter

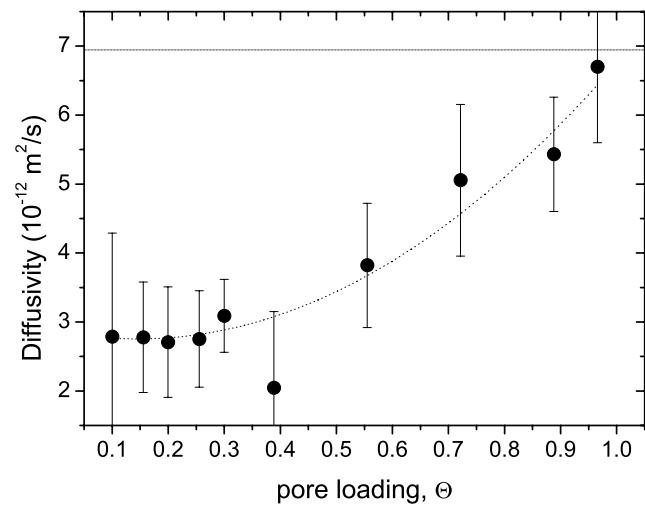


Fig. 5 Diffusivities of TEHOS as a function of the overall pore loading by the cyclohexane-TEHOS mixture. The horizontal line shows the diffusivity of pure TEHOS in Vycor porous glass at full pore saturation. The dotted line is guide to the eye

are always confined to diffuse within this layer in an immediate contact with the pore walls. Therefore, the mobility of TEHOS is almost not affected by the presence of cyclohexane molecules. Further saturation leads to the formation of domains of capillary-condensed cyclohexane, where TEHOS molecules may escape from the surface layer and diffuse more quickly in the pore interiors. The more such regions are formed, the higher diffusivity are obtained for TEHOS.

As it was anticipated in the introduction, with this type of studies we hoped to probe microscopic details of the fluid distribution along the host system. With the data so far obtained, the diffusion behavior is seems to be simply determined by the amount of the capillary-condensed phase, where an enhancement of TEHOS mobility does occur. Thus, this effect prevails over fine details of a particular fluid distribution. In order to further clarify this issue, we have performed diffusion studies at different diffusion times from a few to hundreds of milliseconds. The hope was to obtain patterns typical of restricted diffusion possibly originating from finite exchange rates between capillary-condensed domains and regions with multi-layered molecules (Valiullin et al. 1997, 2004). However, no such dependencies have been found within the experimental uncertainty. This reveals that the exchange rates between different regions are high. Most presumably this is due to the small pore size, which results in the thickness of the surface layers comparable to the pore size.

With the present study, it is possible to determine the ratio of the diffusivities of the two components as an important quantity for their separation by the porous material under study. Figure 6 shows this ratio as a function of the pore loading. It worth noting that this ratio represents the

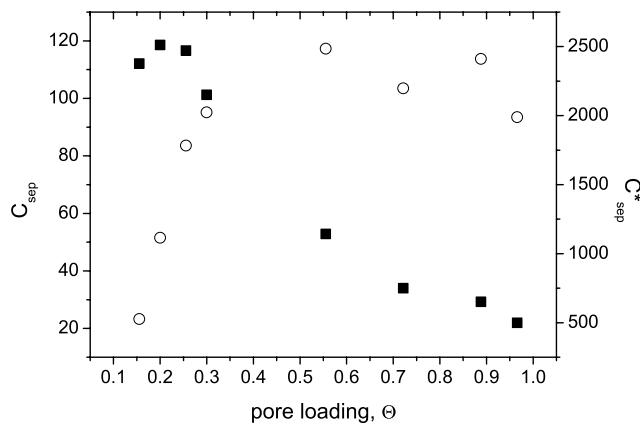


Fig. 6 Separation factors C_{sep} (left axis, filled symbols) and C_{sep}^* (right scale, open symbols) for the cyclohexane-TEHOS binary mixture as a function of the pore loading

diffusion-separation factor C_{sep} for mixtures of two isotopes (Haul 1954). Otherwise, the transport diffusivities have to be used instead. In our case, the latter are not straightforward to determine (Valiullin et al. 2006). Therefore, one may use the ratio of the self-diffusivities only as an estimate for the separation factor.

It is evident that, due to the different dependencies of the diffusivities of the liquid components on the pore loading as shown by Figs. 4 and 5, C_{sep} grows quickly with decreasing pore loading. If one takes account of the changing densities also determining the overall mass transfer, the separation factor may be noted as $C_{sep}^* = \rho_C \theta_C D_C / \rho_T \theta_T D_T$, where ρ and θ refer to the liquid density and pore filling factor of the mixture components. C_{sep}^* is also shown in Fig. 6. Evidently, it does not change appreciably down to about half pore filling and decreases at lower loadings due to decreasing θ_C which, at these conditions, dominates over the increasing diffusivity.

4 Conclusions

Molecular self-diffusivities in a binary liquid consisting of two types of molecules with a large difference in their vapor pressures, namely cyclohexane and TEHOS, in Vycor porous glass have been measured using pulsed field gradient NMR. Pore loadings have been varied by changing the external gas pressure (predominantly given by that of cyclohexane) while keeping the loading of TEHOS constant at 10 volume percents. Diffusivities of the two liquid components have been found to exhibit opposite dependencies on pore loading. This fact is attributed to different physico-chemical properties of two liquid used. In particular, at partial pore loadings cyclohexane, as a liquid with sufficiently high vapor pressure, can explore the pore interiors containing the gaseous phase via Knudsen diffusion. Thus, by increasing

the volume available for the gaseous phase and by increasing density of cyclohexane molecules there, the transport of cyclohexane can be enhanced. In contrast, because TEHOS molecules cannot escape into the gaseous phase, domains filled with the gaseous cyclohexane do form additional geometrical obstacles for TEHOS. Therefore, the diffusivity of TEHOS decreases with decreasing pore loading. These tendencies in the transport behavior may be used to tune membrane separation via tuning the phase equilibrium.

In this preliminary study we aimed at using big probe molecules as a mean to explore fluid distribution in random pores at partial pore fillings. It has been shown that this may in principle be possible by a careful choice of the main sorptive and the host material. In our case, we did not find any patterns of restricted diffusion. We do relate it to the small pore size of the porous glass used. Because of this, TEHOS molecules may easily diffuse between domains of the capillary-condensed phase and domains containing surface layers at the pore walls and the gaseous phase at the pore interiors. To increase the transport resistance between such domains, the use of porous material with bigger pores would be of some help. The use of the main sorptive with a lower vapor pressure (to decrease the thickness of the surface layers) will presumably not solve the problem because the TEHOS diffusivity is almost constant in the region of multi-layer and sub-monolayer adsorption.

Acknowledgements The author acknowledge the German Science Foundation (DFG) for financial support.

References

- Cotts, R.M., Hoch, M.J.R., Sun, T., Markert, J.T.: Pulsed field gradient stimulated echo methods for improved nmr diffusion measurements in heterogeneous systems. *J. Magn. Reson.* **83**, 252–266 (1989)
- Elmer, T.H.: Porous and reconstructed glasses. In: *Engineered Materials Handbook*, vol. 4, pp. 427–432. ASM, New York (1992)
- Galvosas, P., Stallmach, F., Seiffert, G., Kärger, J., Kaess, U., Mäger, G.: Generation and application of ultra-high-intensity magnetic field gradient pulses for nmr spectroscopy. *J. Magn. Reson.* **151**, 260–268 (2001)
- Haul, R.A.W.: Separation of isotopes by means of surface diffusion in porous media. *Naturwissenschaften* **41**, 255–256 (1954)
- Hellweg, T., Schemmel, S., Rother, G., Brulet, A., Eckerlebe, H., Findenegg, G.H.: De-mixing dynamics of a binary liquid system in a controlled-pore glass. *Eur. Phys. J. E* **12**, S1–S4 (2003)
- Jähnert, S., Müter, D., Prass, J., Zickler, G.A., Paris, O., Findenegg, G.H.: Pore structure and fluid sorption in ordered mesoporous silica. I. Experimental study by in situ small-angle x-ray scattering. *J. Phys. Chem. C* **113**, 15,201–15,210 (2009)
- Kainourgiakis, M.E., Kikkilides, E.S., Stubos, A.K., Kanellopoulos, N.K.: Simulation of self-diffusion of point-like and finite-size tracers in stochastically reconstructed vycor porous glasses. *J. Chem. Phys.* **111**, 2735–2743 (1999)
- Levitz, P., Ehret, G., Sinha, S.K., Drake, J.M.: Porous Vycor glass: The microstructure as probed by electron microscopy, direct energy transfer, small-angle scattering, and molecular adsorption. *J. Chem. Phys.* **95**, 6151–6161 (1991)

Naumov, S., Valiullin, R., Monson, P.A., Kärger, J.: Probing memory effects in confined fluids via diffusion measurements. *Langmuir* **24**, 6429–6432 (2008)

Page, J.H., Liu, J., Abeles, B., Herbolzheimer, E., Deckman, H.W., Weitz, D.A.: Adsorption and desorption of a wetting fluid in Vycor studied by acoustic and optical techniques. *Phys. Rev. E* **52**, 2763–2777 (1995)

Pasaogullari, U., Wang, C.Y.: Two-phase transport and the role of micro-porous layer in polymer electrolyte fuel cells. *Electrochim. Acta* **49**, 4359–4369 (2004)

Tuchlenski, A., Uchytík, P., Seidel-Morgenstern, A.: An experimental study of combined gas phase and surface diffusion in porous glass. *J. Membr. Sci.* **140**, 165–184 (1998)

Valiullin, R., Furo, I.: Low-temperature phase separation of a binary liquid mixture in porous materials studied by cryoporometry and pulsed-field-gradient nmr. *Phys. Rev. E* **66**, 031508 (2002)

Valiullin, R., Skirda, V.D., Stapf, S., Kimmich, R.: Molecular exchange processes in partially filled porous glass as seen with nmr diffusometry. *Phys. Rev. E* **55**, 2664–2671 (1997)

Valiullin, R., Kortunov, P., Kärger, J., Timoshenko, V.: Concentration-dependent self-diffusion of liquids in nanopores: A nuclear magnetic resonance study. *J. Chem. Phys.* **120**, 11,804–11,814 (2004)

Valiullin, R., Kortunov, P., Kärger, J., Timoshenko, V.: Surface self-diffusion of organic molecules adsorbed in porous silicon. *J. Phys. Chem. B* **109**, 5746–5752 (2005)

Valiullin, R., Naumov, S., Galvosas, P., Kärger, J., Woo, H.J., Porcheron, F., Monson, P.A.: Exploration of molecular dynamics during transient sorption of fluids in mesoporous materials. *Nature* **443**, 965–968 (2006)

Veith, S.R., Hughes, E., Vuataz, G., Pratsinis, S.E.: Restricted diffusion in silica particles measured by pulsed field gradient NMR. *J. Colloid Interface Sci.* **274**, 216–228 (2004)

Wiltzius, P., Bates, F.S., Dierker, S.B., Wignall, G.D.: Structure of porous Vycor glass. *Phys. Rev. A* **36**, 2991–2994 (1987)