

## Adsorption and Self-Diffusion of Water and Benzene Molecules Adsorbed in Synthetic Opal Samples

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### 1. Introduction

Synthetic opals are a perspective material for creation of photonic crystals [1] and various nanocomposite materials on the basis of spatially-ordered dielectric matrix [2]. The opal samples consist of closely packed monodispersed nano - spheres of amorphous SiO<sub>2</sub>. The diameter of the SiO<sub>2</sub>-spheres depends on the synthesis conditions and can change from several tens up to a thousand nanometres. In the present work adsorption and translational mobility of water and benzene molecules in opal samples have been studied (diameter of spheres 260 nm) – both in the initial state and after annealing at 1293 K. According to electron microscopy and electron-positron annihilation data the porous system of the opals under study includes macropores up to 100 nm and nanopores (ultramicro pores) of 1 nm order.

### 2. Results and discussion

The adsorption isotherm of water on the opal sample is of S-type and similar to that of water vapor on microporous adsorbents, in particular active carbons [3]. The comparative method of the analysis of water vapour adsorption [3] specifies existence of ultramicro pores in an initial sample of opal. The annealing of the opal at 1293 K modified the porous structure as reflected by the adsorption and translational behavior of water.

The stimulated spin-echo pulsed sequence [4] has been used in the PFG NMR measurements. The self-diffusion coefficients (SDCs) of water and benzene in the pores of the synthetic opal before and after annealing were studied as a function of the pore filling and temperature. The temperature of measurements varied from 258 up to 303 K. The maximum value of PFG,  $g = 50$  T/m, allowed the observation of a diffusional attenuation of the spin-echo amplitude over three orders. The duration of PFG,  $\delta$ , varied from 0.08 up to 0.2 ms. The SDCs have been measured at different diffusion times  $t_d$  from 6.5 to 100 ms.

The diffusional echo attenuation measured as a function of the PFG value,  $A(g^2)$ , of water in the sample of the initial opal occurred to be dependent on the temperature and the pore filling. At the low temperatures, from 258 up to 283 K, the shape of  $A(g^2)$  in the opal sample with a pore filling factor  $\theta \sim 0.1$  indicates the existence of non-freezing water in the pores of the opal (Fig.1). The observed attenuations  $A(g^2)$  were approximated by two exponentials with two corresponding SDCs, as follows:

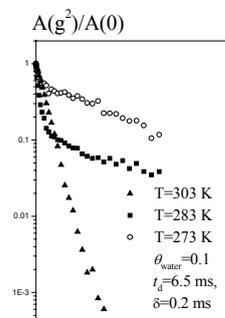


Fig. 1: The diffusional attenuation of the spin-echo of water in the opal at different temperatures.

$$A(g^2) = p_1 \exp(-(\gamma \delta g)^2 t_d D_{\min}) + p_2 \exp(-(\gamma \delta g)^2 t_d D_{\max}), \quad p_1 + p_2 = 1.$$

The values  $D_{\max}$  were attributed to the water molecules in the void space between the nano-spheres and differed by over an order from the  $D_{\min}$  that characterized the mobility of the water in the ultra-micropores.

The minimum SDC occurred to be dependent on  $t_d$  and varied from 6.5 to 100 ms indicating the effect of restricted diffusion of the water molecules in the pores. There was no influence of  $t_d$  on the values of  $D_{\max}$  and  $p_1$ . Hence at low temperatures up to 283 K, the conditions of slow molecular exchange between the two types of pores were valid.

The increase of the temperature up to 303 K caused a change in the observed function  $A(g^2)$  from two-exponential to single – exponential attenuation with one SDC (Fig.1). These changes in  $A(g^2)$  are due to the transfer from slow to fast molecular exchange between the ultra micropores and pores formed by the void space between the nano-spheres. The same effect has been observed when the pore filling factor increased up to complete filling of the pores.

The observed function  $A(g^2)$  for benzene confined in the initial opal samples occurred to be exponential with the SDC exceeding that for water at all temperatures of measurement and pore fillings. So the ultra micropores occurred to be inaccessible for benzene under all conditions.

A single SDC characterized water in the annealed opal samples over the whole temperature interval and pore filling factors under study. The SDC of water in the annealed opal exceeded that in the initial sample. The obtained SDC data confirmed the adsorption data indicating the collapse of the ultra micropores due to annealing.

The temperature dependences of the SDC of water and benzene in the opal samples with pore filling  $0.2 \leq \theta \leq 1$  presented as a function of  $\ln D$  vs.  $10^3/T$  occurred to be linear. The estimated activation energies of water self-diffusion in the opal samples before and after annealing were found to be close to each other and to the value of bulk water, as well.

### 3. Conclusion

PFG NMR self-diffusion measurements of water in opal samples revealed two phases of adsorbed water with differing SDCs attributed to the two types of porosity in the sample. The smallest SDC characterized the mobility of water molecules in the ultra-micropores on the surface of opal nano spheres. Molecular exchange between these two phases became faster as the temperature and pore filling by water increased. The ultra-micropores turned out to be inaccessible for benzene. The annealing of opal at 1293 K induced a collapse of the surface ultra-micropores.

### References

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