N-heptane adsorption and desorption in mesoporous materials

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Abstract. Positron Annihilation Lifetime Spectroscopy (PALS) was used for an \textit{in situ} monitoring of adsorption and desorption processes. The disordered and ordered porous silica as well as the porous polymer were used as adsorbents, while an adsorbate in all the cases was \textit{n}-heptane. The lifetimes and particularly the intensities of the ortho-positronium (o-Ps) components depend strongly on the adsorbate pressure. The analysis of these dependencies allows us to identify several processes, which are taking place during sorption. At low pressure, an island-like growth of the first layers of the adsorbate on the silica, in a contrary to a swelling of the polymer, is observed. A size of the pores, which remain empty, is estimated at the subsequent stages of the adsorbate condensation and evaporation. The adsorbate thrusting into micropores is deduced at \( p/p_0 > 0.6 \) whilst the mesopores are still not completely filled.

1. Introduction
Numerous applications of porous solids require a knowledge of their pore structure. The most popular methods of pore characterization base on an analysis of physical adsorption/desorption of a gas (usually nitrogen at 77 K). In order to determine a pore size distribution, the sequence of calculations like Barrett-Joyner-Halenda (BJH) scheme \cite{1} or non-localized density functional theory (NLDFT) \cite{2}, arising from models of sorption process has to be performed. The accuracy of results depends on the correct interpretation of adsorption/desorption isotherms. Most methods of an isotherm analysis were developed basing on measurements of macroscopic quantities (usually the volume of adsorbed liquid) and a theoretical modelling (conventionally, the Kelvin equation of the classical thermodynamics is used). Still, an interpretation of the results often requires a supposition that the ideal course of pore filling and emptying was distorted by some processes \cite{3,4}. A cavitation, pore blocking, free volume formation at the liquid-solid interface and changes of the condensate density are among them. However, an experimental observation of these effects is a real challenge. This can be achieved only by alternative methods for the adsorption porosimetry, such as small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS) or PALS. The last technique is the most promising one, because it is sensitive directly to the free volumes, such as pores, which are not filled by an adsorbate or subnanometer free spaces present among others on the liquid-solid interface. Moreover, introducing an adsorbate to a sample does not hinder the PALS measurement in any way.

The PALS studies of adsorption and desorption and the accompanying processes were already performed for \textit{n}-heptane adsorbate and several porous silica adsorbents \cite{5-9}. The conclusions derived
from comparison of the most representative results and the results of the measurement performed for porous polymer adsorbent are presented in this paper.

2. Experimental

2.1. Materials

Three porous materials with different pore structures and compositions, but the comparable porosity (pore size, specific surface and total volume) were used as adsorbents (Table 1). The ordered porous silica SBA-15 was prepared following the procedure reported in [7,10]. The tetraethyl orthosilicate (Sigma-Aldrich) as the silica source and the amphiphilic triblock copolymer Pluronic P123 (BASF) as the structure-directing agent were used in the synthesis. The silica gel Si-A was prepared according to the procedure described in [8,11] with the use of Amberlite XAD7HP (ROHM & HAAS, now Dow Chemical Co.) as a porous polymer template. The porous polymer Amberlite XAD4 is commercially supplied by (ROHM & HAAS). N-heptane of purity 99.5% (Fluka) was used as an adsorbate.

Table 1. Parameters characterizing the porosity of the investigated samples obtained from nitrogen adsorption/desorption at 77K: specific surface of the pores $S_{BET}$, total pore volume $V_p$, average pore diameter from BJH for a desorption isotherm $D_{av}$. An arrangement of pores was determined from TEM images.

| Sample  | $S_{BET}$ (m$^2$/g) | $V_p$ (cm$^3$/g) | $D_{av}$ (nm) | Ordered | Material |
|---------|---------------------|------------------|---------------|---------|----------|
| SBA-15  | 1029                | 1.24             | 5.4           | yes     | silica   |
| Si-A    | 1135                | 1.06             | 3.5           | no      | silica   |
| XAD4    | 898                 | 1.27             | 5.5           | no      | polymer  |

2.2. Methods

The powder samples were poured to a loosely closed container fastened inside a vacuum chamber, equipped in a gas dosing system. Prior to the adsorption experiment the samples were kept in vacuum ($\sim$10$^{-4}$ Pa) for about 24 h. A 0.5 MBq $^{22}$Na positron source sealed in an 8 µm Kapton envelope was placed in the middle of each sample. Before $n$-heptane (Fluka, 99.5% purity) was allowed to permeate the sample, it was degassed by freezing in liquid nitrogen followed by pumping out impurities while $n$-heptane was slowly melting. This procedure was repeated three times. Series of PALS measurements at various $n$-heptane pressures from zero to vapor pressure (increasing and then decreasing) was conducted at room temperature.

A standard ‘fast-slow’ delayed coincidence spectrometer was used to collect the positron annihilation lifetime spectra. The spectrometer was equipped with BaF$_2$ scintillators. Each spectrum has been measured for 8 hours, which was enough to collect 1.5-2.0 $\times$ 10$^7$ counts. A high counting rate was obtained at the expense of the resolution, which had to be approximated by two Gaussians (typically with FWHM of about 290 ps and 450 ps, and a contribution of 80% and 20% respectively).

The PALS spectra were analyzed using the LT 9.2 program [12]. In order to decrease a number of fitted parameters, the lifetime of para-positronium was fixed at 125 ps. The free positrons lifetime was varied from 350 to 480 ps depending on a material investigated and whether its pores were filled with $n$-heptane or not. In addition to these short-lived components, three ortho-positronium components were fitted during the analysis. The lognormal distribution of lifetimes was assumed for the longest-lived component. A width of the distribution was described by a dispersion parameter $\sigma$.

3. Results and discussion

Before $n$-heptane introduction to the samples three o-Ps components can be attributed to the structure of the pore walls ($\tau_1 \sim 1.5$-2 ns), micropores ($\tau_4 \sim 6$-10 ns) and mesopores ($\tau_5 > 80$ ns) respectively. Almost all o-Ps in the studied porous materials annihilate in mesopores (Fig.1). The intensities of two
short-lived components in both silica are approximately 1%. Only in XAD4 they reach about 3% each. This situation changes distinctly when \( n \)-heptane fills the pores. Reaching the vapor pressure results in a disappearance of the mesopore related component (‘mesopore component’) in all cases except SBA-15, but even there it decreases to 1%. The major origin of the short-lived components becomes different, i.e. \( n \)-heptane – pore wall interface (‘interface component’, still \( \tau \approx 1.5-2 \) ns) and bubbles created by o-Ps [13] in liquid \( n \)-heptane (‘liquid component’, \( \tau \approx 3.7 \) ns).

Figure 1. The intensities of the o-Ps components related to \( n \)-heptane – pore wall interface (\( I_3 \)), liquid \( n \)-heptane (\( I_4 \)) and mesopore (\( I_5 \)) in SBA-15 (left) Si-A (middle) and XAD4 (right) as a function of \( n \)-heptane pressure relative to its vapor pressure during adsorption (full triangles) and desorption (open triangles).

The intensities of o-Ps components are much more sensitive to \( n \)-heptane adsorption comparing to the lifetimes. An interchange of intensities between the mesopore component (\( I_3 \)) and the liquid component (\( I_4 \)) is visible in Fig.1 as almost mirror reflection of these intensities dependency on relative pressure. This is a clear confirmation of filling initially empty pores (giving contribution to the mesopore component) by \( n \)-heptane (contributing to the liquid component). The shape of a \( I_4 (p/p_0) \) dependency is different for each material. This is caused by a differences in their pore size distributions (the larger the pore, the greater pressure is required for an adsorbate condensation inside of it). Almost vertical \( I_4 \) increase between 0.5 and 0.6 in SBA-15 proves practically a uniform pore size in this material. On the contrary, in Si-A \( I_4 \) starts to change at a very low pressure (~0.1) and
The Si-A structure can be similar, because it is synthesized using the polymer template similar to probability that a positron-electron pair correlated in a spur or blob what is expected to be a structure of pores in XAD4: free spaces left between polymer filled spheres.

XAD4. However, in this case a predominance of very small entrances is which are narrower than the pore i

structure. Still, the hysteresis is too large in Si-A and XAD-4 to be explained this way. In these two samples the pressure at which desorption begins is probably determined by the size of pore entrances, which are narrower than the pore internal size (‘ink-bottle’ pores). This hypothesis is consistent with what is expected to be a structure of pores in XAD4: free spaces left between polymer filled spheres. The Si-A structure can be similar, because it is synthesized using the polymer template similar to XAD4. However, in this case a predominance of very small entrances is expected, because the greatest $I_3$ decrease during desorption is observed at $p/p_0 = 0.2-0.3$.

Although $I_3$ dependencies on relative pressure are almost mirrored of $I_4$, there is a distinct difference at the relative pressure below 0.2 (0.1 in Si-A). No significant change of $I_4$ is observed in this range, while $I_3$ increases in both silica or decreases in polymer by several percent. There can be several causes of a change of the positronium formation probability, among them the most probable is a development of the pore surface. A greater surface roughness of a pore wall leads to a higher probability that a positron-electron pair correlated in a spur or blob [14] encounters the surface during its diffusion-like movement. In a consequence, the probability of a bulk leaving by the pair, followed by Ps formation in a pore, increases. The surface would develop in silica if the adsorbate, instead of forming layers, builds island-like structures. On the other hand, such structures on a polymer surface are not expected, because n-heptane initially penetrate between a polymer chains causing the material swelling. In this case most of the gaps between polymer chains close and the surface becomes smoother.

Similarly, a presence of small hysteresis loops between the adsorption and desorption run of $I_3$ at low pressure in the silica can be explained on the basis of a surface roughness. This is unlikely that island-like structures formed during adsorption appear also during desorption. More probable is that during evaporation the surface of the adsorbate covering pore walls is pretty smooth. Thus $I_3$ is smaller at low pressure during desorption comparing to adsorption, when the surface is more rough.

The shortest-lived component the interface component is related to an annihilation site, which is competitive to bubbles in n-heptane, i.e. both the interface component and the liquid component increase when the mesopore component decreases. This site was identified a priori as an n-heptane – pore wall interface. An argument for such identification is the $I_3$ increase at pressure lower than pressure of the $I_4$ increase. This is in agreement with an unquestioned scenario, where an n-heptane layer (discontinuous isle-like during adsorption) forms before condensation during adsorption or remains after evaporation during desorption. However, this straightforward interpretation of the interface component is most likely simplified. It should be noticed, that o-Ps annihilates not necessarily in the same place, where it was formed. If there is a connection between free volumes, o-Ps can migrate from one free space to another [15]. The direction of positronium migration is mostly from a smaller to larger free volume, because it is energetically favorable. Keeping in mind this effect we can suppose, that o-Ps formed in pore walls (mostly in micropores) gives its contribution to the interface component instead of the mesopore component, when the walls become at least partially covered by an adsorbate. This explains the slope of the $I_3$ pressure dependency in SBA-15 in the pressure range below the adsorbate condensation.

The origin of the hysteresis loop in the $I_3$ pressure dependency in Si-A can be also explained by taking into account the o-Ps migration. The high $I_3$ value (~15%) during adsorption is most likely the result of an annihilation of o-Ps formed both directly in the interface and in micropores connected with
the interface. Because o-Ps formed in the micropores cannot migrate to mesopores, which was the case without adsorbate, they annihilate with the lifetime specific for the interface component. However, above $p/p_0 = 0.6$ n-heptane is pushed into the micropores, what results in decrease of $I_3$ to about 8%. During desorption the micropores remain filled until n-heptane is removed from the pore surface at $p/p_0 < 0.2$, so there is no contribution from them and $I_3$ remains constant. The origin of $I_3$ changes in XAD4 is partly different. Already relatively high $I_3$ increases mostly due to a change of the concentration of a free spaces between polymer chains caused by a swelling. Only about 2% increase above $p/p_0 = 0.1$ can be attributed to the origin similar as in the silica.

Figure 2. The diameter at a maximum of mesopore size distribution ($D_{\text{max}}$) and the full width at 1% of the maximum of the highest distribution ($FWPM$) in SBA-15 (left) Si-A (middle) and XAD4 (right) as a function of the relative n-heptane pressure during adsorption (full triangles) and desorption (open triangles).

The complementary information to the one provided by the intensities can be obtained from an analysis of the lifetimes, especially the longest-lived one proportional to the mesopore sizes. The relation given by the Extended Tao-Eldrup model [16] can be used to calculate pore sizes from lifetimes, but in order to obtain full information provided by positron lifetime spectra both an average lifetime and a dispersion have to be taken into account. Therefore, the lognormal shape of a lifetime distribution defined by an average lifetime and a dispersion was transformed into a pore size distribution according to the calculation scheme described in ref. [5]. Finally, the position of the maximum of a mesopore size distribution ($D_{\text{max}}$) and the full width at 1% of the maximum of the highest distribution for a particular material ($FWPM$) were calculated (Fig.2). The $FWPM$ was used to obtain a width of a size distribution at a constant level for the whole pressure range.

The pore sizes $D_{\text{max}}$ calculated from PALS data for empty pores are in a fairly good agreement with the nitrogen adsorption/desorption results (Table 1) excluding SBA-15. Most likely in SBA-15 the lifetime specific for inter-particle spaces (i.e. the spaces within a conglomerate of randomly oriented structures of hexagonally arranged pores, which forms a powder grain) instead of primary cylindrical pores is observed. This is the result of o-Ps migration outside the straight and relatively wide primary pores.
pores. Also very large FWPM is inadequate for pores of a uniform size. Thus no useful information can be obtained from these data. In other samples an increase of \( D_{\text{max}} \) with pressure is observed. It is the expected dependency, which confirms filling of the smallest pores in the first during adsorption and emptying them in the last during desorption. The increase is not preserved at relative pressure above 0.55 during adsorption in Si-A. It indicates a predominance of the pore narrowing over the closure of the smallest ones. This effect is weaker in XAD4, where \( D_{\text{max}} \) stabilizes only. Such a change of the slope of the \( D_{\text{max}} \) against pressure dependency is visible during desorption in any sample. This is another confirmation of different shape of \( n \)-heptane meniscus during evaporation in comparison to condensation.

A width of the distribution (FWPM) shows some increase at low pressure. This can be related to a change of the pore structure due to the swelling in the polymer (FWPM almost doubled), while its origin in the silica is uncertain (but in this case the increase is much smaller). Above the low pressure increase a plateau in FWPM is observed. A pressure increase in this range results in a shift of the pore size distribution towards larger sizes without a change of its width. A closure of the smallest pores is expected as was already mentioned, but a simultaneous appearance of large ones is difficult to explain. It may be a result of fixing the lognormal shape of lifetime distributions. If a real shape is different (e.g. its maximum is shifted towards greater diameters comparing to the maximum of the lognormal distribution), such a distortion may cause an artificial broadening of the distribution. Nevertheless, above the pressure at which \( I_4 \) decreases to about a half of its highest value, FWPM begins to decrease as expected. This indicates the closure of consecutive groups of pores of a certain (the smallest ones still remain open) size. The changes of FWPM during desorption are shifted towards a lower pressure following the hysteresis observed in \( I_4 \) and \( I_5 \).

4. Conclusions
A PALS adsorption study provides numerous additional information about the studied material in comparison to a classic adsorption experiment. A pore structure determination based on the shape of the \( I_4 \) pressure dependency and the hysteresis loop provides practically the same information as a volume of adsorbed \( n \)-heptane in the classic experiment. Additional information about the initial growth or the final decay of the adsorbate layers on adsorbent surface is provided by \( I_5 \). A presence of a hysteresis in a \( I_4 \) pressure dependency can indicate presence of micropores. Probably an adjustment of an adsorbate molecule size may allow to detect micropores of various minimal sizes. The strength of the adsorbent-adsorbate interaction may also be important in a study of this effect. A direct measurement of a size of the free space, which is still free of adsorbate, allows us to verify the adsorption/desorption models.

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