

PALS and DSC study of nanopores partially filled by hexadecane

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Abstract. The controlled porosity glasses (CPG) filled with various amount of hexadecane (HXD) in nanopores were studied both by the positron annihilation lifetime spectroscopy (PALS) and the differential scanning calorimetry (DSC) methods. Two types of CPG matrices were used with average pore sizes 12.6 and 22.2 nm. The PALS measurements showed, that when the process of large pores filling by HXD has started, the long o-Ps lifetime went down to HXD o-Ps lifetime about 3ns [1]. DSC measurements at partially filled nanopores showed always two crystallization peaks [2]. Their positions depended on average pore size of matrix. Third crystallization peak was identified in overfilled samples (only short o-Ps lifetimes were present) and their position in temperature scale was the same as for the bulk HXD peak. The latter peak was independent of the average pore size of matrices. This fact confirms the assumption that processes studied by PALS with the samples that contained smaller amount of HXD in CPG occurred inside of nanopores of the matrix.

1. Introduction

In our previous PALS study of confined molecules of hexadecane (also called cetane) in fully filled silica gel pores we found some basic differences between dynamics of bulk and confined hexadecane in wide temperature range from 15 K to 300 K [1]. While the free-volume hole size decreased sharply in bulk HXD at 292 K and then no change for low temperature region has appeared the slow change was observed of the free-volume hole size with decreasing temperature was observed in case of confined HXD. Similar differences were reported in [3]. DSC measurements indicated two crystallization peaks (one for confined state with the position depending on the pore size and one for the bulk state with a stable position in temperature range) [1]. Presence of two crystallization peaks [2] for the confined hexadecane in CPG samples evokes the questions, what induces these different states, where they are localized, etc. The second interesting point is process of successive filling (or release) of materials to (from) nanopores utilized for instance at drug release. The aim of this work was to look for some relationships between quantity of hexadecane in partially filled nanopores of CPG samples with different pore size and positron lifetime or DSC parameters.

2. Experimental

Samples of liquid n-hexadecane, with the chemical formula $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$, was obtained from



Lachema, Czechia. Melting point of hexadecane is 292 ± 0.1 K [2], molar mass is $226.45 \text{ g mol}^{-1}$, density is 0.773 g mL^{-1} and length of molecule is app. 2.2 nm. Controlled porosity glasses CPG-10 with 12.6 nm and CPG-10 with 22.2 nm mean pore diameter, respectively were obtained from BDH Chemicals Ltd., England. Porous glass was filled by a defined amount of HXD at ambient temperature. The actual amount of HXD was controlled by weight with precision of ± 0.01 wt.%. The quantity of hexadecane in CPG is characterized by the coefficient of filling k defined as $k = m_{\text{HXD}} / (m_{\text{CPG}} + m_{\text{HXD}})$, where m_{HXD} and m_{CPG} is mass of HXD and CPG in sample, respectively.

The powdered samples were located in two aluminium containers, which were placed on both sides of the Na-22 positron source (Kapton foil, cca 1.7 MBq activity). Positron annihilation lifetime spectra were measured by standard fast-fast coincidence method using plastic scintillators and XP2020 photomultipliers. The time resolution of system was ~ 320 ps. This was assessed by the defect-free Al sample, employing three Gaussian approximations of resolution function. PATFIT-88/POSITRONFIT [4] code was used for the analysis of spectra. Source correction was taken into account.

PALS measurements were performed in vacuum 2 Pa (continuous pumping) and at temperature 300 K. Time of each measurement was about 24 hours. The escape of hexadecane from the sample was less than 2 wt. %. This was confirmed by the weight of samples before and after measurements.

Differential scanning calorimetry (DSC) is the principal thermo-analytical method which, by measuring the enthalpy evolved or absorbed by the investigated sample, indicates the change of thermodynamic state of sample, namely the onset ($T_{x,s}$) and minimum ($T_{p,s}$) peak temperatures and heat of the solidification (ΔH_s) or of the melting of hexadecane ($T_{x,m}$, $T_{p,m}$, ΔH_m). Power-compensation DSC8500 (Perkin-Elmer) with automatic intracooler (203 K), encapsulated samples of 15 – 50 mg and dynamic argon atmosphere were used. The scanning rate was $\pm 2 \text{ K.min}^{-1}$.

3. Results and discussion

The five-component analysis of lifetime spectra was performed for a better differentiation of o-Ps lifetime. Two shorter o-Ps lifetimes were near to value of bulk hexadecane about 3ns [1]. The PALS measurements have indicated that the large pores alter their apparent size above $k \sim 0.2$ for (Figs. 1 and 2). This corresponds to about 40% and 30% pore saturation for CPG 12.6 and CPG 22.2, respectively - as estimated from the pore volume given by producer and the weight of HXD added.

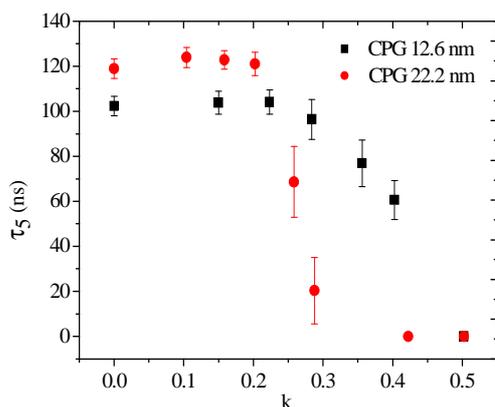


Figure 1. Dependence of lifetime τ_5 on the coefficient of filling k .

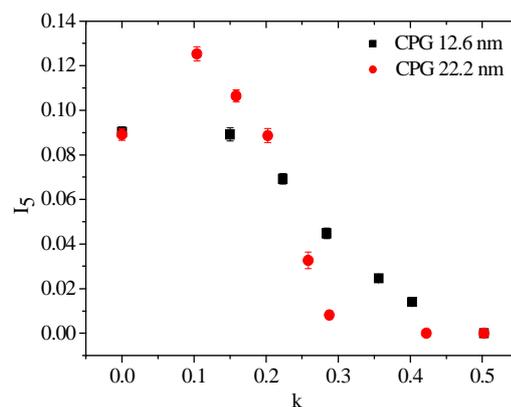


Figure 2. Dependence of relative intensity I_5 on the coefficient of filling k .

The CPG 22.2 nm is fully filled above $k=0.3$, while CPG 12.6 nm with greater surface of pores is fully filled at approx. $k=0.5$. Presence of two shorter o-Ps lifetimes (Fig.3,4) in two distinct matrices (1.4 ns, at 8% and 4.5 ns, at 0.4% for CPG 22.2 nm, as well as 1.7 ns, at 4.9% and 7.4 ns, at 1.5% for CPG 12.6 nm) caused some difficulties in the interpretation of PALS spectra in the ns region. These

lifetimes correspond to the free volume of matrix skeleton similar to [5], and are overlapped with the o-Ps lifetime of HXD for filled samples. As evident from Fig. 5, the increase of HXD amount in CPG is accompanied with the growth of intensity of the sum of I_3 and I_4 .

At small k values, the HXD molecules may be situated as continuous or discontinuous thin film on the inner pore walls and they do not affect value of τ_5 . Shorter o-Ps lifetimes connected with the free volumes of disordered molecules HXD in the film or free volumes between HXD molecules and CPG walls are larger than lifetime of HXD in full-filled pore. It is in accordance with some ideas of work [5], about the behaviour of o-Ps lifetimes at adsorption and desorption of n-heptane on porous silica gel at pressure measurements.

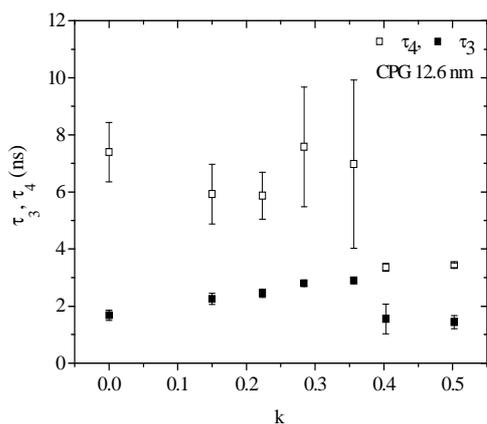


Figure 3. Lifetime τ_3 and τ_4 for different coefficient of filling k . CPG 12.6 nm.

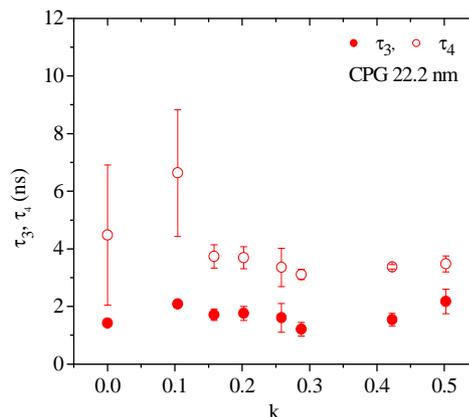


Figure 4. Lifetime τ_3 and τ_4 for different coefficient of filling k . CPG 22.2 nm.

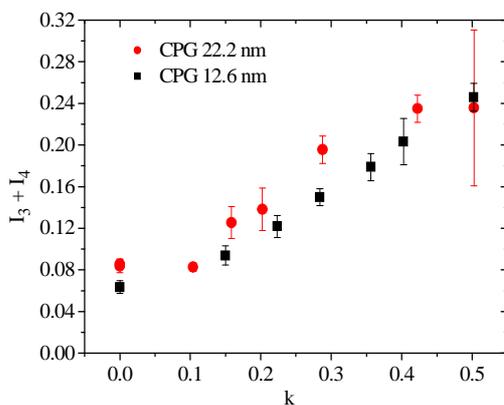


Figure 5. Sum of I_3 and I_4 for both CPG for different k .

Three independent phase transition peaks were observed in each DSC measuring cycle. One crystallization exotherm Rb of the bulk HXD was observed only in the overfilled samples. Its position on the temperature scale is the same as for the bulk sample. Two crystallization sub-peaks Rc1 and Rc2 belong to the confined HXD in the case of continuous cooling (Fig. 6). Temperatures of both Rc1 and Rc2 transitions decrease with the decreasing pore diameter of CPG. Similar situation appeared with other samples exhibiting different pore size [6]. Transition temperature is a function of $1/R_p$ (R_p – radius of matrix pores, Gibbs-Thompson rule). The onset temperature of both transitions Rc1 and Rc2 is independent of k .

Influence of extent of pore-filling k on the total enthalpy of solidification of hexadecane confined in CPG is manifested in Fig. 7. The

peak area for bulk hexadecane [2] is larger than areas of all peaks for the HXD confined in CPG. This difference is expressed as $|\Delta H|$ in %. $|\Delta H|$ is calculated as the difference of ΔH between -219.5 J g^{-1} (measured for the bulk HXD sample) and the sum of all three solidification heats, namely of Rb, Rc1 and Rc2 for the confined systems. This apparently missing HXD might indicate that not entire HXD present in pores takes part in the crystallization process. This deficit decreases with increasing k .

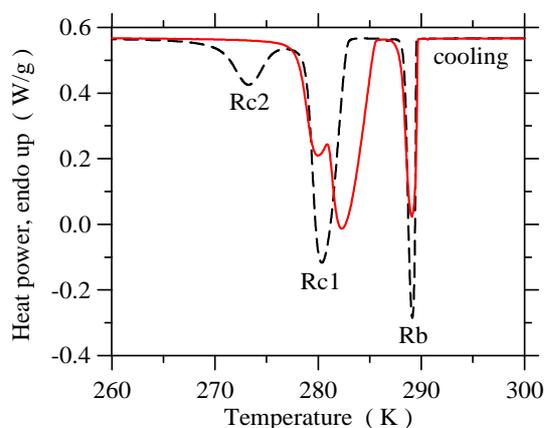


Figure 6. DSC cooling curves for hexadecane confined in CPG (diameter of pores 12.6 nm - - and 22.2 nm ____). The scanning rates were $\pm 2 \text{ K min}^{-1}$.

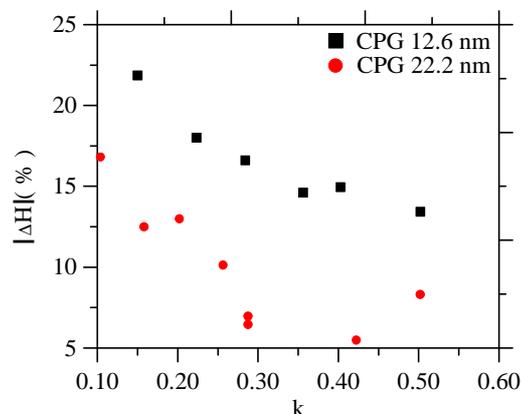


Figure 7. Difference $|\Delta H|$ between bulk hexadecane and total enthalpy of all DSC crystallization peaks in CPG sample for different k .

4. Conclusions

The PALS measurements showed that hexadecane filled up pores. The process of the filling of the large pores has started approx. at $k \sim 0.25$ and 0.30 for CPG 22.2 nm and 12.6 nm, respectively. Long o-Ps lifetime decreases at large filling coefficient k to the value 3.4 ns, close to the typical HXD o-Ps lifetime about 3 ns. In comparison with bulk HXD, the arrangement of HXD molecules in fully filled pores is partially disordered. This is similar to silica gels [1]. At small k values, the HXD molecules may be situated as thin film on the inner pore walls. They do not affect value of o-Ps lifetime τ_5 . Due to strong capillary forces, their location on the outer surface of CPG particles is improbable.

Two crystallization sub-peaks Rc1 and Rc2 are observed by the DSC measurements in the process of cooling for hexadecane confined in CPG. Their onset temperature depends on $1/R_p$ and is independent of k . The absolute value of the enthalpy of both peaks increases with the increasing filling coefficient k . For confined hexadecane, the absolute value of the total solidification enthalpy is always lower than the solidification enthalpy for bulk hexadecane and this difference decreases with increase of k .

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