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Molecular dynamics of 4-*n*-octyl-4′-cyanobiphenyl in partially filled nanoporous SBA-type molecular sieves

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Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

The molecular dynamics of 4-*n*-octyl-4′-cyanobiphenyl (8CB) confined to the nanopores of new SBA-type molecular sieves was investigated in a wide temperature range using broadband dielectric spectroscopy (10^{-2}–10^{9} Hz). One molecular sieve has a hexagonal structure of the pores while the other is a cellular nanoporous material. To explore the extent of surface interaction effects a high and a low filling degree were considered.

For the molecular sieves with a high filling degree two relaxation regions were observed: a bulk-like relaxation process related to molecules, which behave as mesophase, located in the centre of the pores. The second relaxation process has a much lower relaxation rate than the former and is assigned to molecules located in a surface layer. The temperature dependence of its relaxation rates follows the Vogel–Fulcher–Tammann law, characteristic for glassy dynamics.

For samples with a low filling degree only one relaxation process due to the surface layer was observed. Moreover, especially at the temperatures lower than the melting point of bulk 8CB, its relaxation rate is situated between the characteristic frequencies of the two relaxation processes observed for the pores with a high filling degree. This behaviour gives a measure of the extension of the influence of the wall on the neighbouring 8CB molecules. In addition, the differences revealed by the molecule dynamics inside the two types of nanoporous materials are related to both surface interactions and geometrical constraints.

Keywords: Confined liquid crystals; Molecular sieves; Dielectric measurements; Relaxation processes; Glassy dynamics

1. Introduction

The behaviour of molecules confined to restricted geometries has received a considerable attention especially from theoretical point of view in the last years [1–7] due to finite size effects and of the quenched disorder of soft condensed matter including superfluids, random magnets, elastomers and liquid crystals (LCs) [8].

Simple restricted geometries or porous media with large pores such as silica gel, Vycor glass, Anopore, Nuclepore, controlled porous glass (CPG) etc. were mostly employed as host materials. Recently molecular sieves were also used due to their arrays of pores and cavities with known geometries, a high internal surface area, and a chemical as well as mechanical stability. In addition, it was possible to decrease the diameter of the confining pores below 2.5 nm. Molecular sieves with different framework topologies like MFI, FAU, CLO, and MCM-41 were applied as LC hosts [4–11].

Quenched disorder is related mostly to two competing effects such as surface anchoring and finite size effects.

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Their relative role is determined by the size of the pores and the interaction of the guest molecules with the surface: Finite size effects should dominate if the pore size is small [12]. Generally for phase transitions, confinement induced disorder decreases transition temperatures, broadens and lowers the heat capacity peak and may change the order of the transition [12]. It is also expected that confinement and disorder have a considerable influence on the molecular mobility and relaxation processes as well, yielding to a change of the bulk-like relaxation processes and the appearance of a new slow, glassy dynamics due to a surface layer [9b,9c,9d,13,14].

In this contribution, results concerning the reorientational dynamics of 4-*n*-octyl-4′-cyanobiphenyl (8CB)—a well-known LC—confined inside molecular sieves are presented. Two recently synthesized nanoporous molecular sieves of SBA-type were used as hosts with a structure which is quite different to that of CPG membranes or silica gels: One molecular sieve, AlSBA-15 has a hexagonal structure of the cylindrical pores with a mean size of 8.4 nm and a rather narrow pore size distribution. The second host material, SiNMS-F is a cellular foam-like nanoporous material, with a mean pore size of 17.3 nm. Dielectric spectroscopy in a broad frequency and temperature range was applied to investigate the complex dynamical behaviour of 8CB molecules confined inside the molecular sieves in comparison to the bulk. To explore anchoring or surface in comparison to confinement effects samples with different loading degree were investigated.

For pores with a high filling degree, the relaxation processes were due to bulk-like LC, in the centre of the pores and to a surface layer. In the case of pores with a low filling degree (<50%) only one relaxation process was observed attributed to molecules in the surface layer. The differences observed for the molecular dynamics of the 8CB molecules confined to pores with high or low filling degrees are analysed and explained by the extension of the surface–LC interaction. Moreover the results obtained for the different molecular sieved are discussed in the frame of confinement effects.

2. Experimental

8CB was chosen as guest molecule because it is thermally stable. In the bulk 8CB forms LC phases and shows several well-known phase transitions at 294.4 K (C/S_A, 306.7 K (S_A/N) and 314 K (N/I), where C symbolizes the crystalline; S_A, the smectic A; N, the nematic and I, the isotropic state. 8CB was purchased from Aldrich and was used without further purification.

Molecular sieves, either AlSBA-15 or SiNMS-F were hydrothermally prepared by using non-ionic surfactants (poly(ethylene oxide)-*b*-poly(propylene oxide) block copolymers) as synthesis-directing agents and silica and aluminosilicate oligomer species [15] using literature procedures [16,17]. They were calcined at 773 K in air and routinely characterized by XRD, thermal analysis, FTIR spectroscopy, nitrogen absorption and electron (scanning and transmission) microscopy as described in detail elsewhere [11a,15a,18]. The sample AlSBA-15 shows the typical pattern of hexagonally arranged pores (channels), while a cellular structure is found for the sample SiNMS-F. Some texture features of the molecular sieves are given in Table 1.

Table 1
Texture characteristics of confining molecular sieves

Sample	BET surface area (m^2/g)	Mean pore diameter (nm)	Pore volume (cm^3/g)
AlSBA-15	602	8.4	1
SiNMS-F	576	17.2	1.9

Finely grounded powder of these molecular sieves was pressed under low pressure to self-supported pellets of ≈100 μm thickness, which were evacuated under vacuum at 573 K for 8 h to remove water and other volatile impurities. The pores/cavities of the molecular sieves can be loaded with 8CB using either its solution in acetone [18b,19] or a small excess of 8CB in the isotropic state [9] for 1 h. Since the loading of the pores with excess in isotropic state requires a higher amount of 8CB than the method in solution, the solution route is applied here. To obtain samples with different loading levels require further treatments. Firstly the solvent have to be evaporated, secondly the excess 8CB molecules located on extra pores of the grains and on the outer surface have to be removed and thirdly 8CB inside the pores/cavities have to be partially removed. These latter objectives were reached by submitting the sample to a low vacuum (10^{-2} Torr) at 373 K for a definite time: To prepare samples with a high filling degree this time was 1 h. To obtain materials with low filling degree this time was 4–5 h.

The loading/filling degree was estimated by thermogravimetric measurements as already described for other composites [18b] since the organic part is measured by the weight loss up to ≈723 K (it is burning-off up to this temperature) while the molecular sieve resists at higher temperatures (the weight is constant by increasing the temperature up to 1073 K). The thermogravimetric measurements were performed by a Setaram TG-DTA 92 apparatus, under a dry nitrogen atmosphere, using the same samples, which were already measured by dielectric spectroscopy. The content of 8CB c_{8CB} was determined and the loading degree $\Theta = c_{8CB}/(V_{pores}\rho_{8CB}^{conf})$ was estimated by taking the density of confined 8CB as $\rho_{8CB}^{conf} \approx 1\ g\ cm^{-3}$. The samples with a loading degree close to 1 (0.89 for AlSBA-15 samples and 0.98 for SiNMS-F samples) were further called "with a high filling degree" whereas those with the loading degree lower than 0.50 (0.43 for AlSBA-15 samples and 0.15 for SiNMS-F samples) were called samples "with a low filling degree". In the following, the samples were labelled by 8CB(*n*)/MS where *n* is the loading degree and MS is the acronym used for the corresponding molecular sieve.