Experimental report

19/03/2021

Proposal: **CRG-2613** **Council:** 4/2019

Title: Dynamics of Binary Liquids in Mesopores with Periodically AlternatingSurface Interaction

Research area:

This proposal is a new proposal

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Samples:
DVB-PMO : divinybenzenebridged Periodic Mesoporous Organosilica (powder)
Toluene (C_7H_8)
Ter-butanol (C_4OH_{10})

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	7	7	17/06/2019	24/06/2019

Abstract:

Dynamics of Binary Liquids in Mesopores with Periodically Alternating Surface Interaction

General aim of the project: In this study a periodic modulation of the **fluid-wall interactions** was introduced in order to control the dynamics of a prototypical nanoconfined binary fluid (Toluene/Tert-butanol). While nanophase separation of these mixtures has been demonstrated when confined in hydrophilic nanopores, more complex interactions were introduced using Periodic Mesoporous Organosilica (PMO) that were synthesised and studied at Hamburg in the group of M. Fröba. These materials retain the 2D crystalline triangular arrangements of channels of MCM-41 but additionally present a **periodic arrangement of organic and silica units** along the pore axis.

Experiment: In this experiment, Divinyl-Benzene bridged PMOs were used in order to favour hydrophobic interaction with Toluene, while hydrophilic interactions were favoured between Ter-butanol and the surface silanols (Fig. 1).

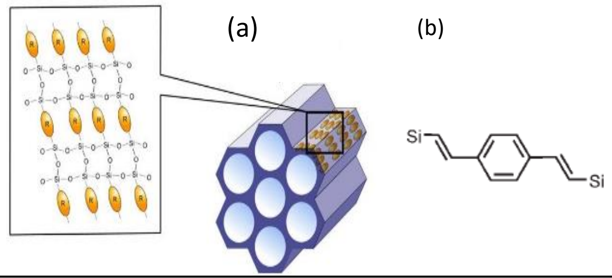

Figure 1. (a) Crystal-like arrangement of alternating silica and bridging organic units R in the pore walls of the mesoporous PMO. Pore diameter=4.1nm, repetition distance=1.2nm (b) Hydrophobic divinyl benzene bridging organic unit (after Hoffmann et al. 2006).

In order to separate the dynamics of the two molecules, binary liquids with different H/D isotopic compositions were used to systematically vary the incoherent scattering cross-section of the 2 components. QENS spectra were acquired at the incident wavelength 5.1Å (res. 70μeV) for the pure TBA (H), the TOL (H), as well as their TBA/TOL binary mixture with 2 isotopic compositions D/H and H/D. Both bulk liquids and liquids confined in the DVB-PMO were studied. We also measured the the empty matrix, that turned out to be essentially elastic.

The summary of the systems and conditions of measurements is provided in Table 1.

	LIQUID COMPOSITION	**TEMPERATURE (K)**
EMPTY PMO MATRIX	-	2, 220, 315
FILLED PMO MATRIX	100% TBAH	2, 180, 220, 250, 315
	50% TBAH / 50% TOLD	
	100% TOLH	
	50% TOLH / 50% TBAD	
	30% TBAH / 70% TOLD	220, 250, 315
BULK LIQUID	100% TBAH	180, 220, 250, 315
	100% TOLH	
	50% TBAH / 50% TOLD	250, 280, 315
	50% TOLH / 50% TBAD	

Data analysis: Standard data corrections were applied using the packages MANTID and LAMP provided at the ILL. The experimental intensity was corrected for detector efficiency, for the background contribution arising from the empty cell and spectrometer, and transformed into the Q and energy dependent scattering function $S(Q,\omega)$. The fitting of scattering functions $S(Q,\omega)$ in the frequency domain was carried out using the QENSH program provided by the Laboratoire Léon Brillouin (LLB, Saclay, France).

Results

The QENS spectra of Toluene filled and Tert-butanol filled DVB-PMO are shown in Fig. 1. Equally good spectra were obtained for the bulk systems and the other mixtures confined in DVB-PMO.

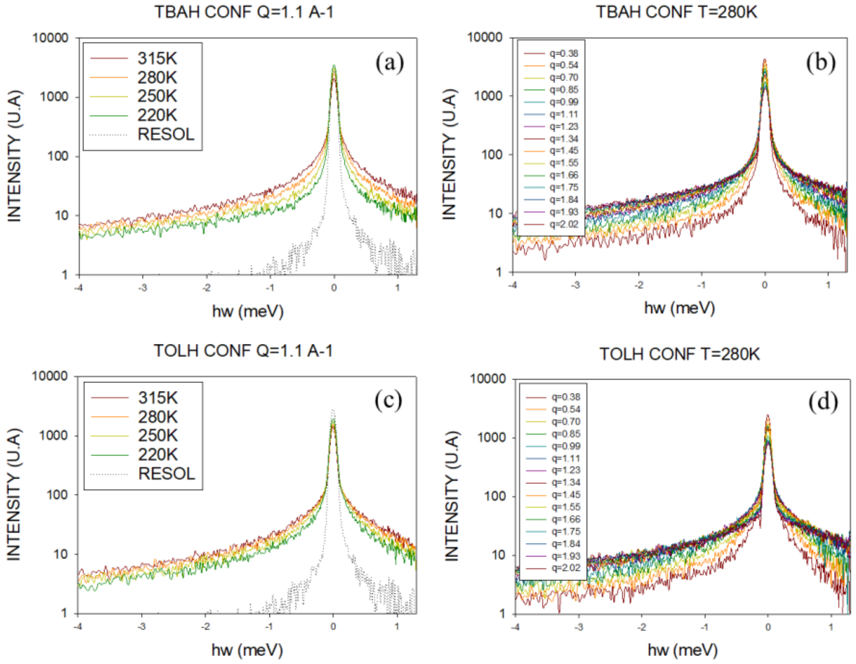

Fig 1. Temperature and Q dependence of the scattering intensity of confined TBAH (above panels) and TOLH (bellow panels) in DVB-PMO. QENS spectra measured on (a, c) at a same Q = 1.1 Å^{-1} and various temperature 220, 250, 280 and 315K, and on (b, d) at a same T = 280K and various Q from 0.38 to 2.02 Å^{-1}.

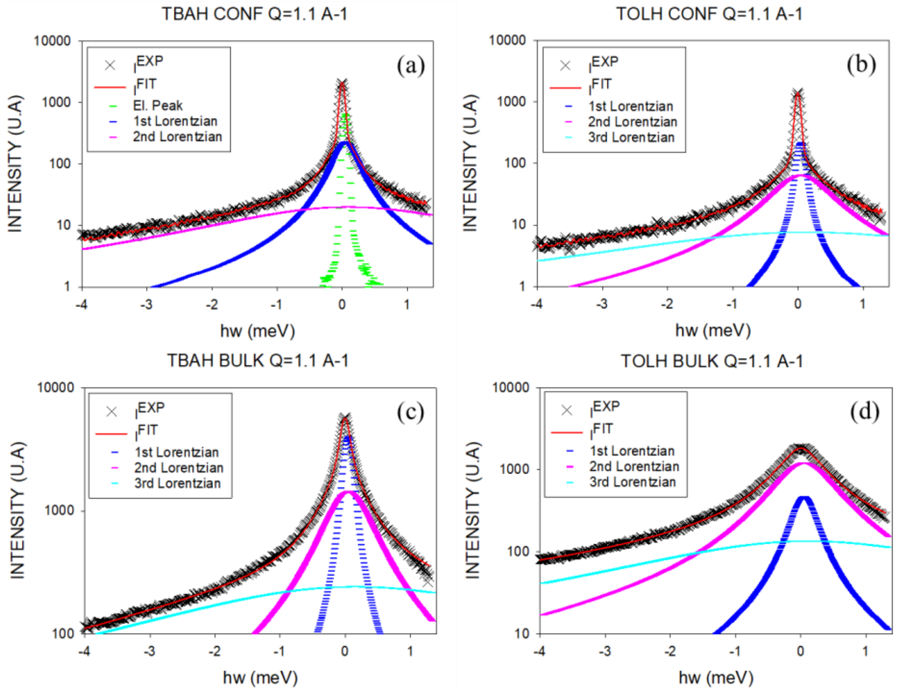

Fig 2. QENS spectra (symbols), fitted function (red solid lines) and its comprising Lorentzian functions and elastic peak (dashed lines) measured for confined TBAH (a), confined TOLH (b), bulk TBAH (c), bulk TOLH (d).

All the spectra of bulk and confined liquids were fitted individually at each Q. For bulk liquids, the best model comprised a sum of three Lorentzian functions (3L) (cf. Eq. 1), while one elastic component, i.e. a Dirac function $\delta(\omega)$, and a quasielastic contribution comprising a sum of two Lorentzian functions (2L+E) was needed for the confined liquids (cf. Eq. 2). It should be noted that for confined liquids, the elastic contribution arising from the pore wall atoms was already accounted for by adding the scattered experimental intensity of the empty matrix of DVB-PMO to the theoretical functions. This means that the persistent elastic contribution was actually ascribed to a fraction of molecules with frozen translational diffusion. The fitted intensities related to the different models can be written as:

$$I^{3\mathrm{L}}(Q,\omega) = [A_T(Q)L_T(Q,\omega,\Gamma_T) + A_S(Q)L_S(Q,\omega,\Gamma_S) + A_F(Q)L_F(Q,\omega,\Gamma_F)]\otimes R(Q,\omega) \quad (1)$$

$$I^{2\mathrm{L+E}}(Q,\omega) = [A_0(Q)\delta(\omega) + A_S(Q)L_S(Q,\omega,\Gamma_S) + A_F(Q)L_F(Q,\omega,\Gamma_F)]\otimes R(Q,\omega) \quad (2)$$

where $A_i(Q)$ is the amplitude of the i^{th} pure elastic component (denoted EISF) describing the geometry of motions and L_i is a Lorentzian function with a linewidth HWHM Γ_i. The comparison between the fitted functions (red solid line) and the experimental QENS spectra (symbol) for bulk and confined TBAH and TOLH in DVB-PMO is illustrated in Fig. 2.

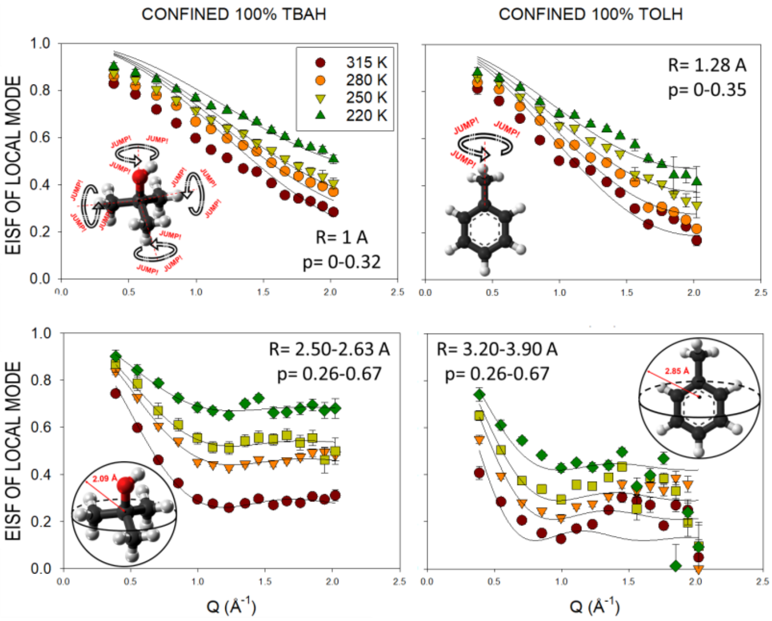

Fig 3. EISF of the fast (upper panels) and slow (lower panels) relaxation modes as a function of temperature for confined TBA H (left panels) and confined TOL H (right panels). Solid lines are fits by theoretical predictions corresponding to the molecular trajectories sketched in inset.

A microscopic picture of the different relaxation modes arising from Eq. 1 and Eq. 2 could be obtained from the fits of the different EISFs with models of molecular motions. This is illustrated for a selection of systems in Fig. 3. The corresponding timescales were evaluated from the width of each quasielastic line.

A comprehensive discussion of the results, showing the synergetic effect of the chemical composition of the mixture and the pore surface chemistry, has been made in an article written by Jani *et al.* to be submitted.