# Experimental report

29/08/2024

**Proposal:** 6-07-112 **Council:** 4/2023

**Title:** Deep Eutectic Solvents in nanopores: Insight into dynamic and structural heterogeneities

**Research area:** Chemistry

**This proposal is a new proposal**


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**Samples:** ETHALINE (H/D) = ethylene glycol / choline chloride (D9) 2:1
MCM-41 = nanoporous SiO2
SBA-15 = nanoporous SiO2
ETHALINE (D/H) = ethylene glycol (D6) / choline chloride 2:1

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN16B | 4 | 3 | 08/03/2024 | 11/03/2024 |
| IN5 | 3 | 3 | 24/11/2023 | 27/11/2023 |
| D16 | 4 | 4 | 30/10/2023 | 03/11/2023 |


**Abstract:**

For the last decade, Deep Eutectic Solvents (DESs) have been the matter of tremendous interest. They exhibit exceptional functional properties, making this emerging class of solvents a very promising new candidate among `green¿ alternatives to classical solvents. Interestingly, most DESs present atypical properties emerging from the formation of nanodomains and dynamical heterogeneity at several length scales, and attributed to the complexation of their ionic and H-bonding molecular constituents. Thus, better understanding the physicochemical properties of DESs at the mesoscopic scale has now become a matter of fundamental interest. Given the significance of interfaces and nanopores in many targeted applications of DESs, the question emerges about the effect of mesoporous confinement on their dynamic and structural heterogeneities. The present project aims at addressing this open question by combining QENS and SANS experiments with in-lab spectroscopies.

**6-07-112 Deep Eutectic Solvents in nanopores: Insight into dynamic and structural heterogeneities**

**Summary** The proposal aimed at addressing confinement effects on the **structure (studied on D16)** and local **dynamics (studied on IN5B and IN16B)** of a prototypical Deep Eutectic Solvent (DES) named ethaline (ethylene glycol EG / choline chloride ChCl) confined in mesoporous silica by SANS and QENS. Ethaline at eutectic composition (EG:ChCl; 2.3:1) with **two symmetric deuterations** has been studied in bulk and confined in **MCM-41** and **SBA-15** silicas with pore size 1.8 and 4.15 nm on the 3 instruments. The effect of different hydration levels was also studied for confined Glycerol on D16. Different isotopic compositions were used, as indicated below, in order to vary the relative coherent scattering length density (for diffraction experiments on D16) and the relative incoherent scattering cross section (for QENS experiments on IN5B and IN16B) of the different components of the mixtures.

All the experiments planned in the project could be successfully performed on D16, IN5B, and IN16B. The data reduction has been finalized. All the results have been modelled and interpretated. We are currently preparing two manuscripts, one concerning the structural study, one concerning the dynamics. All this work will be included as part of the PhD thesis of Nadim Kamar.

**D16 experiments** conducted from 30/10/2023 to 03/11/2023

The accessible Q-range of D16 (Q=0.03 Å$^{-1}$ -> 1.93 Å$^{-1}$) was best-suited for our study that aimed at determining the radial concentration profile of the confined mixtures from the modelling of the intensity of the Bragg reflection from the mesoporous network based on isotopic contrast effects.

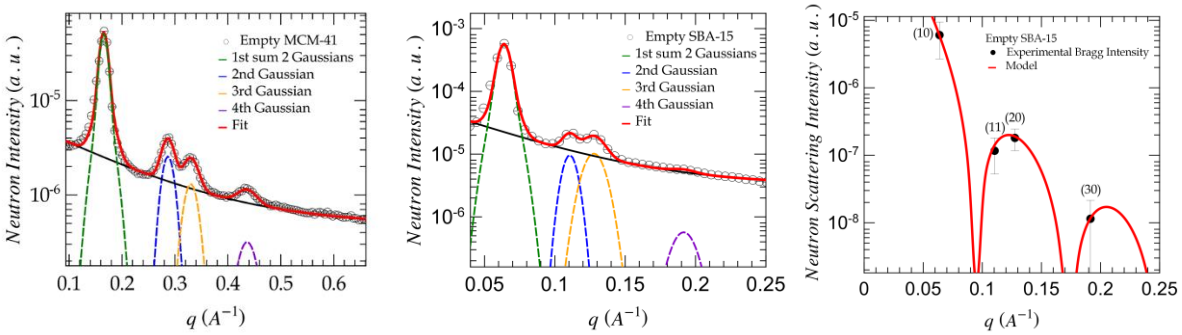


**Fig. 1** Diffraction spectra of the empty matrices. Fit of the Bragg reflection intensity of the empty SBA-15.

The intensity of the Bragg reflection was evaluated from the diffraction spectra of the two empty matrices (Fig. 1) and then fitted using a structural model assuming the form factor of cylindrical pores. Based on the structural parameters obtained from the analysis of the dry matrices, we derived the form factor of a core-shell model with different scattering length density profiles and shell thicknesses. It was fitted to the experimental Bragg reflections of the different systems in order to quantify the non-homogeneous character of the radial concentration of the different confined mixtures. The approached is illustrated in Fig. 2 for one mixture with specific isotopic composition confined in MCM-41. While showing that homogeneous mixing of the confined liquid does not allow to reproduce the measured intensities (green line), consistent predictions were obtained by assuming partial segregation of glycerol at the pore surface. For each sample, the most probable shell thickness, and concentrations in the shell and core were identified through the 2D maps that represent the level of agreement between the modelled core-shell form factor and the experimental results (cf. Fig. 3).

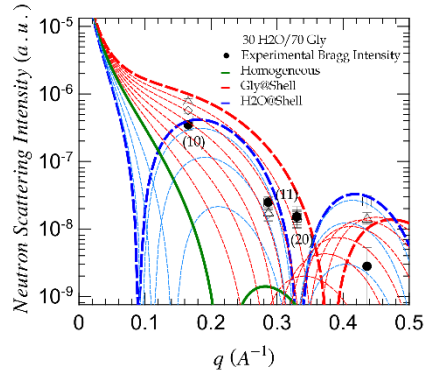


**Fig. 2** Predicted form factor for the confined mixture assuming either homogenous mixing (green line) or partial microphase separation with preferential adsorption of glycerol (red) or water (blue) at the surface, forming layer with different thicknesses.

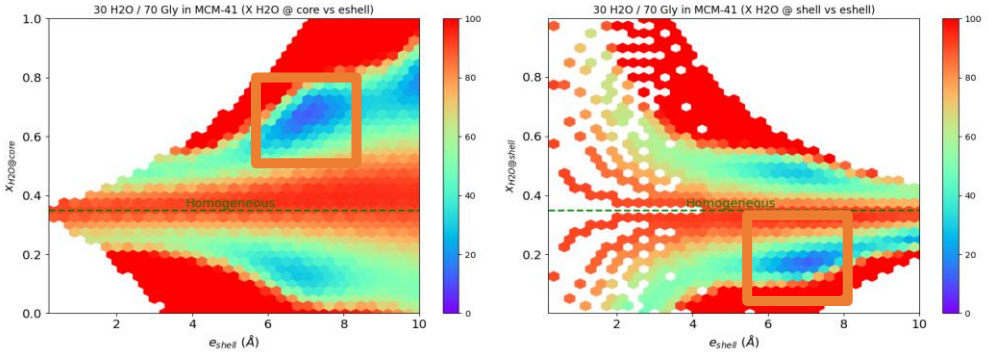


**Fig. 3** Agreement between the modelled core-shell form factor and the experimental results as a function of the shell thickness, and composition of the shell (left panel) and the core (right panel).

**IN5B experiments:** conducted from 24/11/2023 to 27/11/2023

The quasielastic spectra of the DES ethaline were acquired for **two different isotopic compositions** in the **bulk** liquid and in confinement in **MCM-41 and SBA-15**. In addition to standards, we also measured the purely elastic contribution from the two dry empty porous matrices. An ILL orange cryofurnace was used to select **3 different temperatures 298, 325, 350K**. 2 different incoming neutron wavelengths (**4.9Å and 8Å**) were selected in order to vary the elastic energy resolution (resp. 80ueV and 20ueV). The data were reduced using Mantid scripts. The obtained dynamic structure factors were fitted using a 2 Lorentzian-model at each independent Q-value using QENSH software, as illustrated in **Fig. 4**.

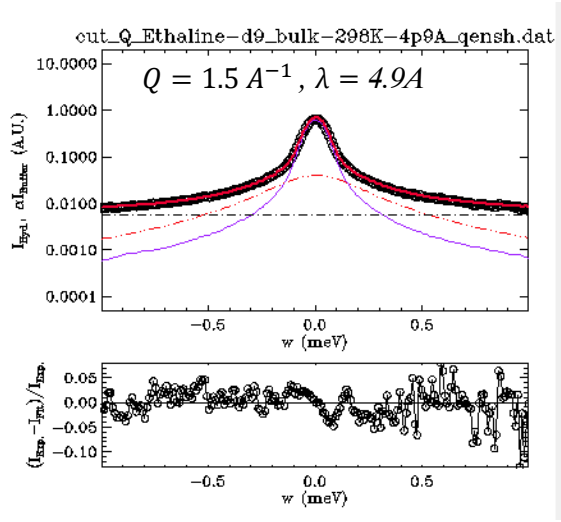


**Fig. 4** The fitted model (solid red line) comprising 2 Lorenzians (dotted-dashed and violet) and one experimental spectrum (symbols).

From these fits, we derived the Q-dependence of the quasielastic broadening of the sharp and broad lines, as well as the EISF of the broad component. The nearly Q-independent quasielastic broadening of the broad component as well as the Q-dependence of its EISF demonstrated that it is related to a fast localized motion (**Fig. 5**). On the contrary, the broadening of the slow component clearly displayed a dispersive character for all samples. It could nicely be fitted with a Singwi–Sjölander (SS) jump diffusion model (**Fig. 6**).

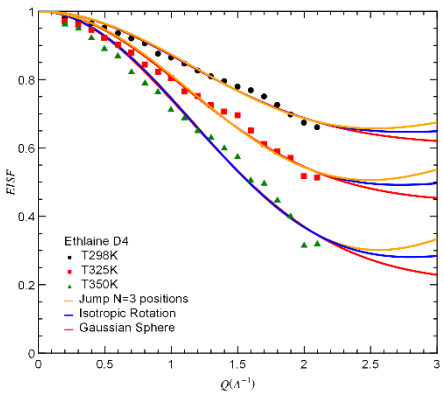


**Fig. 5** Illustration of the Q-dependence of the EISF of the fast component for one DES sample at 3 different temperatures. Lines are fitted models.

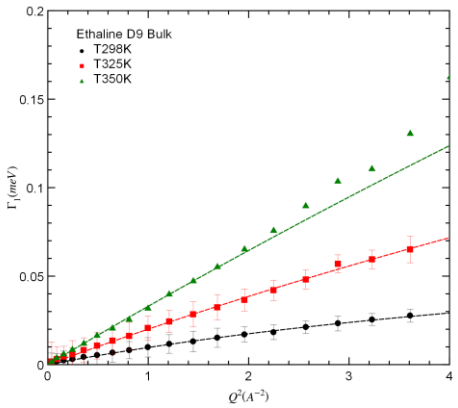


**Fig. 6** Illustration of the Q-dependence of the quasielastic broadening (HWHM) of the slow component for one DES sample at 3 different temperatures. Lines are fitted models.

**IN16B experiments:** conducted from 8/03/2024 to 11/03/2024

The measurements were performed on exactly the same samples as measured on IN5B (i.e. Ethaline DES with **2 different isotopic labelling**, in the **bulk** and confined in **2 different porous matrices**, and also standards and the two dry empty porous matrices). We measured Elastic Fixed Window Scans (EFWS) and Inelastic Fixed Window Scans (IFWS) for 2 different energy off-sets (i.e. 3 ueV and 6 ueV) on the temperature range from 350K to 2K.

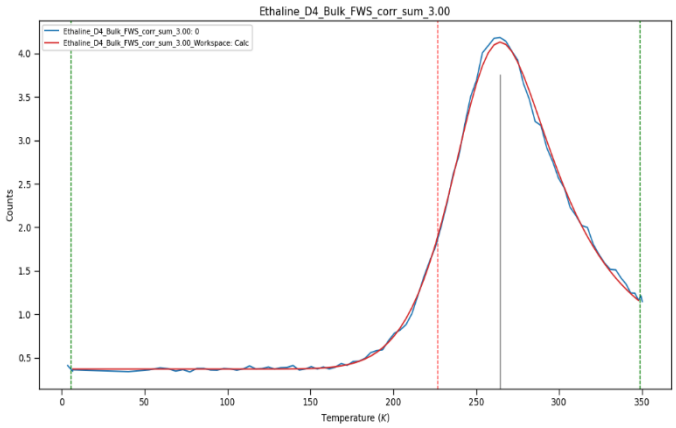


**Fig. 7** Example of Inelastic Fixed Window Scans (IFWS) measured for bulk Ethaline. Experimental intensity (blue line) and fitted model (red line).

The data were reduced using Mantid scripts. Then the scans were fitted assuming that the dynamic structure factor could be modelled by a single Lorentzian, with an Arrhenius temperature dependence of its width, and so its corresponding relaxation time. The choice of this model was justified by the assumption that, given its high energy resolution, only translation motion would contribute within the window of IN16B, while the local mode seen on IN5B would appear as a flat background with negligible intensity. The scans were fitted independently for each Q-value. Excellent quality of fit was obtained as illustrated for one sample in Fig. 7. The assumptions made in the model were a posteriori further justified by the Q-dependence of the quasielastic broadening that followed jump diffusion model, as illustrated in Fig. 8. Moreover, very good agreement was obtained between data acquired on IN5B and IN16B, when the fitted widths from IESF were interpolated to the temperatures at which IN5B experiments were performed.

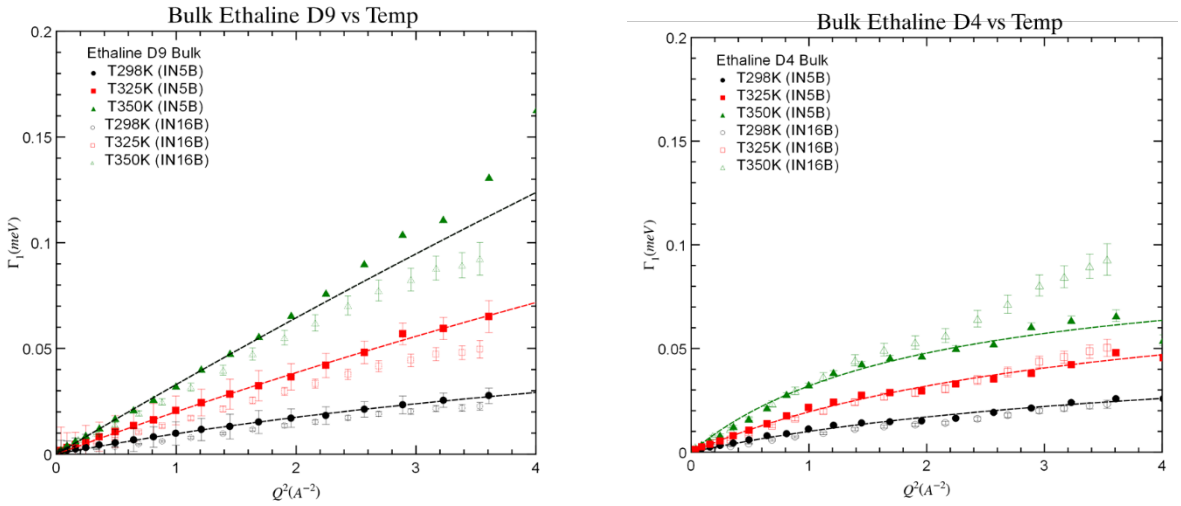


**Fig. 8** Comparison of the quasielatic broadening related to translational diffusion as measured on IN5B and IN16B for different temperatures and isotopic composition.

Combining the complementary resolutions of IN5B and IN16B, we eventually reached an overall description of the translational dynamics on an extended temperature range. Effect of isotopic composition and effect of confinement with different pore sizes could be assessed as well.

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