Experimental report

21/06/2021

Proposal: **6-07-76** **Council:** 4/2020

Title: Transport of water in soft confinement: influence of hydrostatic pressure and mechanical stress

Research area: Materials

This proposal is a resubmission of 6-07-63

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Samples: PIM-1

Instrument	Requested days	Allocated days	From	To
WASP	5	2	24/08/2020	26/08/2020
IN16B Si 111 BATS	3	3	08/03/2021	11/03/2021
IN15	1	1	25/09/2020	28/09/2020

Abstract:

Transport of water in soft porous materials is relevant to a broad range of applications but remains unclear in many aspects because of several effects that have to be taken into account: surface chemistry, diffuse boundaries and deformations or mechanical effects. In the proposed study, we plan to experimentally investigate the interplay between mechanical deformation, structure and transport. On the selected sample of heterogeneous hydrophobicity (PIM, Intrinsic Microporosity Polymer), we will characterize the collective and individual dynamics of confined water on a complementary timescale to previous TOF measurements, under different mechanical loads and hydraulic pressures. For this purpose, we require 3 days on IN16B, 5 days on WASP and 1 day on IN15.

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1. Experiments performed with a nafion (112) film

1.1. Context

According to the proposal which aims at experimentally investigating the coupling between transport and mechanics (matrix deformation) in a soft porous environment, we have performed some measurements on a Nafion film. Indeed, previous measurements (performed on D16, IN6, WASP and IN15) on the initially proposed PIM-1 sample were not successful due to the too high tensile modulus of the polymer, justifying our choice to change the sample and to investigate a softer one. Therefore, we have studied the water dynamics in a nafion film which is subjected to different mechanical constrain (at fulll hydration) and hydrostatic pressures.

1.2. Experimental results

Experiments were performed using a homemade high-pressure cell made of 7075 aluminium alloy. Different conditions have been tested in terms of mechanical stresses (tightening level of the screws of 3, 4 and 5 Nm) and hydrostatic pressures (15 and 300 bars) The $S(\omega)$ spectra obtained at the different experimental conditions demonstrated only negligible differences. Thus, we decided to make first measurements on a complementary study based on a cellulose membrane (see below) in order to make high pressure measurements in the future if the results are conclusive.

2. Experiments performed with a cellulose based membrane

2.1. Context

The cellulose membrane investigated (CDMPC, Figure 1a) has been specially synthetized at the CERMAV laboratory in order to perform chiral separation of a racemic mixture of (R,S)-1-(1-naphthyl)ethanol (Figure 1b). This CDMPC filtration membrane demonstrates enantioselective sorption of the R-enantiomer yielding to a S-enantiomer rich mixture. This chiral separation is poorly understood and the characterization of the molecular mechanisms behind this separation is relevant for chemical and biomedical industries.

2.2. Experimental results

Quasi-elastic neutron scattering (QENS) experiments have been performed on IN16B in order to measure the diffusion coefficients of the different enantiomers in contact with the cellulose based membrane in order to have a better understanding of their interactions with the membrane. The experimental $S(\omega)$ spectra at the different tested conditions are presented in Figure 1c. We note that major differences in the QENS broadening have been observed for low Q-values. Above $Q=0.85$ Å^{-1}, the differences observed in the QENS contribution are negligible, only the intensity is decreasing with Q. The contribution from the dry membrane is purely elastic and can be fitted with a simple Delta function. The dynamical structure $S(Q,\omega)$ has been approximated by the product of the Debye – Waller factor, accounting for the vibrational motions, with the sum of a Delta function and a Lorentzian function accounting for the elastic contribution and the diffusive motions respectively. The obtained Q^2 dependence of the unconstrained Half-Width at Half-Maximum (HWHM) of the Lorentzian function is shown in Figure 2a. The extracted diffusion coefficients calculated with the Fick's equation on the appropriate Q-range are given in Table I.

Table I : Translational diffusion coefficient calculated with the Fick's law

	Solvent	Pur « *S* »	Mixture « *R/S* »
D_T x10^{-5} [cm^2/s]	1.14 ± 0.03	1.62 ± 0.03	1.48 ± 0.02

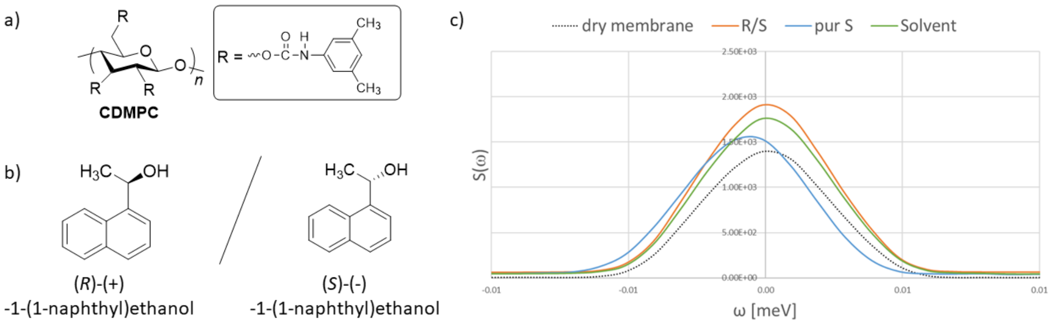

Figure 1 : a) The enantioselective cellulose based membrane investigated: CDMPC (cellulose (3,5-dimethylphenylcarbamate)) b) The racemic (R,S) mixture c) S(ω): sum over the whole Q-range (from 0.64 to 1.88 Å^{-1}) ; excluding the first three detectors Q=0.19, 0.29 and 0.43 Å^{-1}. The empty cell has been subtracted considering 10% scatterers. The following measurements have been performed: dry membrane in black; the membrane + 300 µL deuterated solvent (Acetonitrile/water, 30/70 %vol) in green; the membrane + 451 µL deuterated solvent + 20 mg pur « S » enantiomer in blue; the membrane + 326 µL deuterated solvent + 20 mg racemic mixture of « R/S » enantiomers in orange

The solvent is made of a deuterated mixture of water and acetonitrile. If the dry membrane does not exhibit any quasi-elastic component, it may be very different for the solvated one, due to the presence of the side groups attached to the cellulose backbone (see Figure 1a). The QENS signal from the solvent is therefore arising both from the liquid and from the side chains motions. This is the origin of an averaged diffusion coefficient slower than the matrix containing the enantiomers.

Both *R* and *R/S* containing samples exhibit faster dynamics than the solvated matrix. The diffusion coefficient extracted from the pure *S* sample is faster than the one from the *R/S* sample. This result can be interpreted as being the combination of the *S* enantiomer dynamics with a slower contribution coming from the *R* enantiomer which dynamics is constrained/limited because of its interactions with the membrane. Considering this assumption, we performed a deeper analysis of the data obtained with the mixture *R/S* by fitting the data with a supplementary Lorentzian function on a restricted Q-range from 0.19 to 0.94 Å^{-1}. In this case, the HWHM variation with Q^2 of the first Lorentzian has been fixed according to the value of the D_T (1.77x10^{-5} cm^2/s) found in the previous analysis for the pur *S*. The Q^2-dependence of the HWHM of the two Lorentzian is presented in Figure 2b. We observe a smaller slope for the HWHM variation of the additional Lorentzian corresponding to a diffusion coefficient of 0.84x10^{-5} cm^2/s. This very slow dynamics is attributed to the *R* enantiomer, in agreement with its expected slower dynamics. The extracted signal corresponds however still to a translational motion, not a rotational one that would account for tightly trapped molecule.

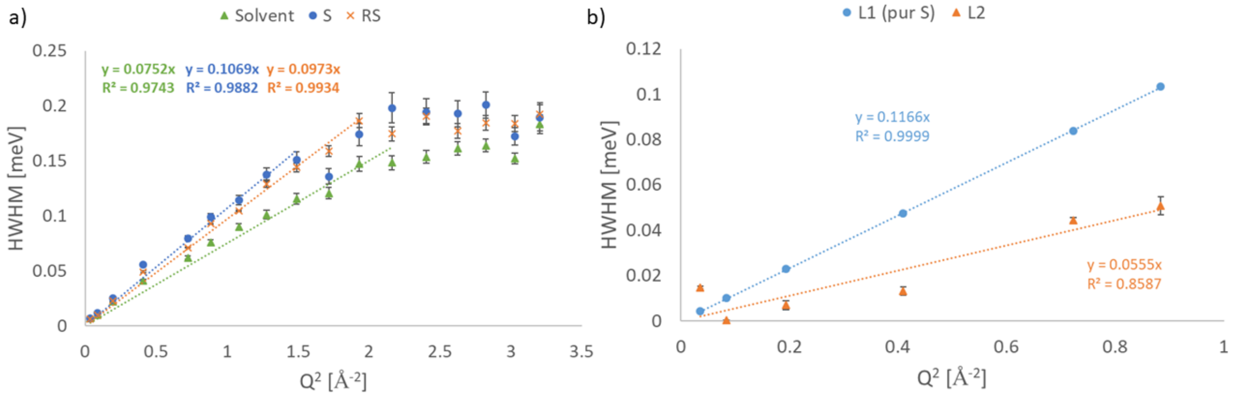

Figure 2 : HWHM variation as a function of Q^2 a) fits with only one Lorentzian function b) fits with two Lorentzian function in the case of the « R/S » mixture