Experimental report

23/11/2017

Proposal:	**6-07-14**	**Council:**	10/2016

Title: How does the chemistry of lipids influence the behaviour of interlayer water ?

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
CH3(CH2)12 COOH, myristic acid
ac-1-Myristoylglycerol
1,2-dimyristoyl-sn -glycero-3-phospho-(1-rac -glycerol) (sodium salt) (DMPG)
1,2-dimyristoyl-3-trimethylammonium-propane (chloride salt) (DMTAP)

Instrument	Requested days	Allocated days	From	To
IN5	3	2	13/02/2017	15/02/2017

Abstract:

The phase diagram of confined water below 273 K is not only influenced by the confinement, but also by the presence of solutes or ions, the surface chemistry or the confining matrix elasticity. These factors have a drastic influence on the sorption (or desorption) of water when increasing (or decreasing) the temperature between 200 and 273 K, leading to macroscopic water diffusion in some systems and not in others. The mechanisms for such behaviour are still poorly understood.

We propose to address this question in investigating the phase behavior of water in lamellar lipid arrangements, in which water is confined between bilayers over thicknesses of ~0.3-2 nm. Lipid bilayers present ideal systems to study the effects of ions and surface chemistry on the water melting point and diffusion coefficient.

On four selected lipid systems with different headgroups and similar tails, we will measure on IN5 simultaneously the diffusional dynamics, the ice diffraction pattern and the interlamellar spacing as a function of temperature. The experimental results will enable to evaluate the different thermodynamical contributions to the water melting point. We require 3 days of beam time.

Experimental report on exp. 6_07_14
How does the chemistry of lipids influence the behavior of interlayer water ?
M.Plazanet, J. Peters, B. Coasne

Background and scope of the experiment

The scope of this experiment was to characterize the dynamics of water confined between lipid bilayers at sub-zero temperatures. Based on previous studies and examples from the literature, we expect the phase diagram and mobility of nano-confined water in soft matrices to depend on several factors that we aim at addressing separately: (i) **Confinement**: what is the effect of characteristic size of confinement on the phase diagram of water? (ii) **Electrolytes**: what is the role of solutes and ions? (iii) **Poromechanics**: what is the role of membrane elasticity/rigidity? What is the pressure associated with internal crystallization? (iv) **Surface**: what is the role of surface chemistry?

In this experiment, we therefore investigated the role of surface chemistry with different lipids: myristic acid (MA), rac-1-Myristoylglycerol (MG), Dimethyldioctadecylammonium (DDAB), 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) and 1,2-Dimyristoyl-*sn*-glycero-3-phosphoryl-glycerol (DMPG) (see figure 1).
All samples were equilibrated in H_2O or D_2O in a 100% humidity chamber during 24h at 40° C. We then reached the following hydrations:
DMPC-H_2O: 4.2 water molecule/lipid; DMPC-D_2O : 3.5 water molecule/lipid
DMPG-H_2O: 4.1 water molecule/lipid; DMPG-D_2O: 4.0 water molecule/lipid;
MA, MG, DDAB: 0 water molecule/lipid (no hydration), dry sample only.

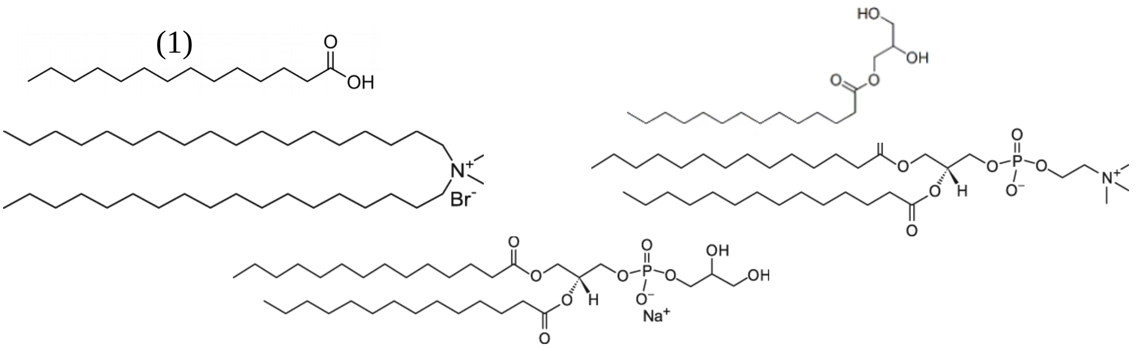

Fig.1: (1) MA, (2) MG, (3) DDAB, (4) DMPC and (5) DMPG.

IN5-Diffraction.

To separate the dynamics of the lipids and the water, we measured on IN5 at the energy resolution of 50 μeV the spectra from DMPC and DMPG hydrated both in H_2O and D_2O as a function of temperature, and MG and DDAB hydrated in H_2O at room temperature, only.
On figure 2 are represented the coherent structure factors S(Q) of. all measured samples At 295 K, the correlation peaks arise from the lipid organization, in the horizontal (high Q) and vertical (low Q, interlamellar spacing) directions. We note from figure 2 (left) that both MG and DDAB samples, that do not adsorb water, are more structured than DMPC and DMPG. Decreasing the temperature, we observe the shifting of the lipid correlation peaks toward higher Q values, as expected. We could observe the diffraction peak from ice only in the DMPG-D_2O sample at the lowest temperature, as shown on the right side of the same figure.

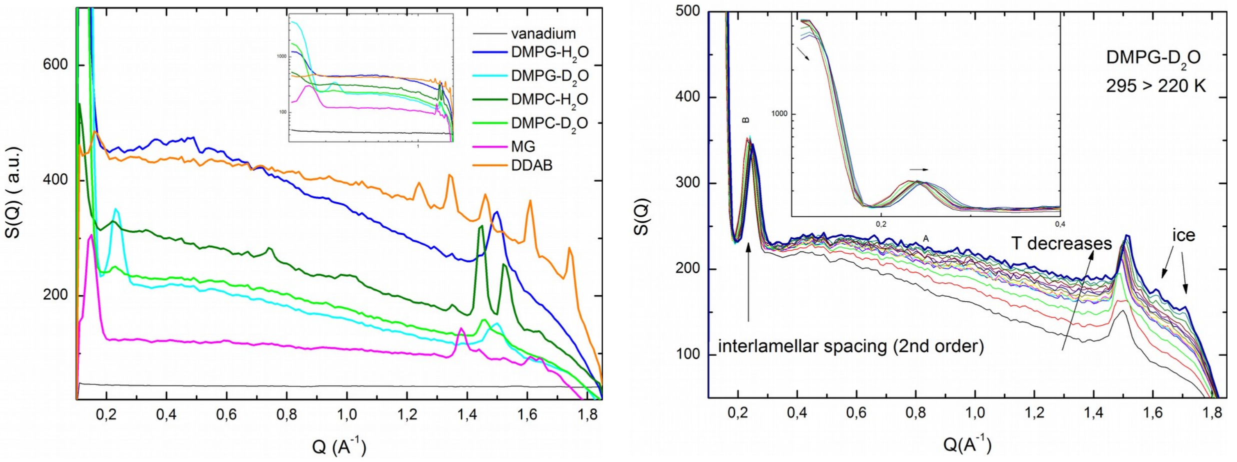

Fig. 2: S(Q) measured on IN5 at 295 K for all the samples, and as a function of temperature on DMPG-D_2O.

IN5 - QENS

All samples were measured at 295 K, and DMPC and DMPG have been characterized over the full temperature range. The signal was quite strong in DMPC and DMPG but much weaker in the MG and DDAB samples. However, the signal of those last samples could be analyzed in the same way. Various models have been considered to fit the QENS signals. A first phenomenological analysis based on the sum of an elastic and two Lorentzian contributions showed that no long range translational motion could be observed. More sophisticated models based on combinations of isotropic rotation and/or confined translational diffusion in ill-bonded confinement could not provide any significant results. The main reasons for that is an increase of the QENS signal at small angles (for 2theta < ~9°), and a quite asymmetric signal. We therefore based our analysis on a two-Lorentizans' model. All samples provided similar results: a strong elastic contribution, and two Lorentzian contributions with rotational/localized dynamics' characteristics (increasing intensity with Q, constant full width hall maximum (FWHM(Q)), one with FWHM~ 0.08 meV, the second one with FWHM~ 1.5 meV (see figure 3). Because of the similarities between the H2O and D2O hydrated samples, we assign the two contributions to the lipid dynamics.

Under cooling, the intensities decrease, while the widths tend to increase, as observed in the plot of the DMPG-H_2O characteristics on the figure below. This trend is an indication of a potential that becomes deeper, more rigid, when the temperature decreases.

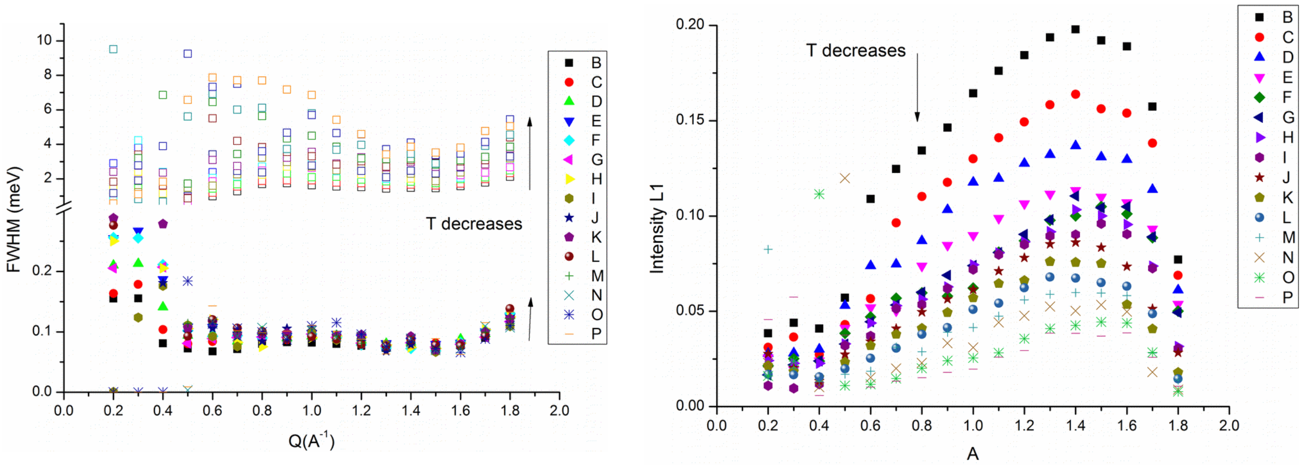

Fig. 3 : FWHM of both Lorentzian contributions in DMPG-H2O sample as a function of temperature (left), similar to what is observed in all samples. ON the right part of the figure are plotted the intensities of the slowest contribution.