Experimental report

09/02/2016

Proposal: **6-02-506**

Council: 4/2012

Title: Counterions dynamics in a model charged porous system

Research area: Soft condensed matter

This proposal is a resubmission of 6-02-493

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Samples: SiO2 in water, TMACl

Instrument	Requested days	Allocated days	From	To
IN16	5	5	10/11/2012	15/11/2012

Abstract:

The objective is to study the dynamics of the counterions in a charged porous medium, which is part of a larger project which couples multiscale experiments and simulations in order to identify the factors which control the dynamics of charged species in porous media (ANR Dypolypo). The model porous system is made of charged silica spheres assembled in dense assemblies. We now control the charge of the walls of the porous and the size of porosity through volume fraction. Hydrogenated tetramethylammonium (TMA) counterions in D2O allow to study the dynamics of the counterions from incoherent scattering. Previous measurements by TOF (MIBEMOL, LLB) show some quasielastic signal for TMA however long times are missing so that the dynamics of TMA counterions cannot be completely determined. It is essential to use a higher resolution technique, such as backscattering, to access the slow dynamics of the counterions.

Counterions dynamics in a model charged porous system

Experiment 6-02-506

Context

The aim of this experiment was to contribute to the understanding of the dynamics of the counterions in a charged porous medium. It was part of a larger project which involves both multiscale numerical simulations and experiments in order to identify the key factors controlling the dynamics of charged species in a charged porous medium (ANR Dypolypo : *Modelling the DYnamic properties of POLYelectrolytes in charged POrous media*). Few studies deal with the dynamics of counterions especially at this local nanometric scale and the multiscale approach is seldom used. The experimental, as well as the theoretical studies available so far do not deal with particles or porous media but mainly with polyelectrolytes.

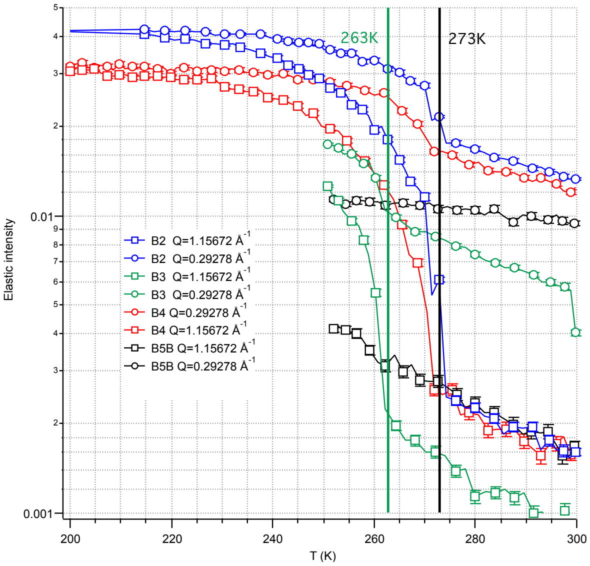
The model system used here is a porous medium made of charged silica spheres concentrated in dense assemblies using osmotic stress. This model system is appealing since silica is ubiquitous in natural porous media and such particles are commercially readily available. We are now able to control not only the charge of the walls of the porous medium but also the volume fraction of solid and therefore to modify the average porosity.

Sample preparation

In addition, we can prepare systems where the main incoherent scattering contribution comes from the counterions by exchanging the initial Na^+ counterions for hydrogenated TetraMethylAmmonium (TMA^+) counterions and using D_2O as a solvent instead of H_2O as shown by former SANS measurements. The structure, already studied by SANS, is that of a colloidal glass and shows no contribution of the silica particles beyond $Q = 0.25\ \text{Å}^{-1}$. A sufficient amount of TMA counterions can be achieved (for reasonable sample thicknesses, i.e. reasonable transmissions) with a large enough solid/liquid interface in the porous medium, accessible with small nanosilicas (diameters 5 – 8 nm). This was checked experimentally with titration of the surface charge of the porous media. The silica nanoparticle surface charge was varied from $-20\ \text{mC m}^{-2}$ up to $-100\ \text{mC m}^{-2}$ known from acid base titration. Above this value of surface charge density the silica starts to dissolve noticeably.

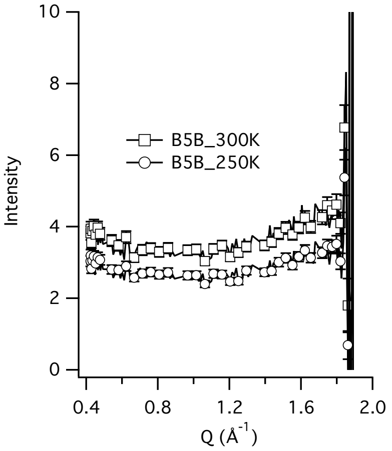
Elastic scan with temperature:

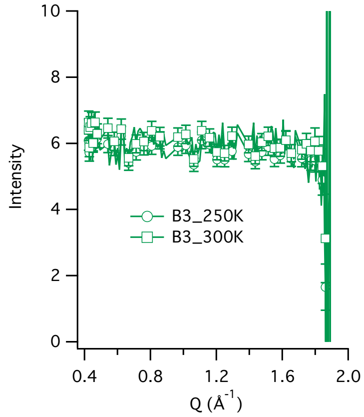
The elastic peak evolution with temperature is reproduced below. The increase of signal with the decrease of temperature show the slowing down of the dynamics. One noticeable step is observed for the freezing of water at 273 K. The only notable departure for this overall behaviour is seen for highly concentrated sample (volume fraction, $\phi = 0.30$, sample B5) and light water sample (B3).

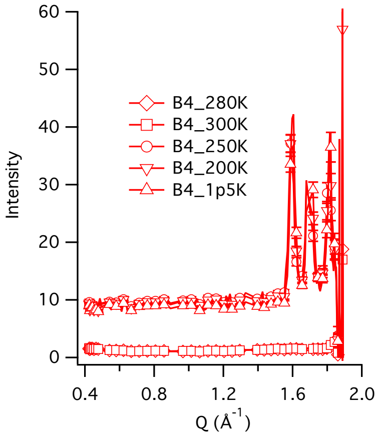


Diffraction:

The diffraction measurement with temperature is reported below. For the light water sample, the signal is dominated by the flat incoherent signal of hydrogen. For diluted samples or where the concentration of counterions is not high enough, the peak of ice are clearly observable at low temperatures (see for example sample B4). However, for the most concentrated sample, only the high *Q* structure of amorphous silica coming form the nanoparticle is seen.

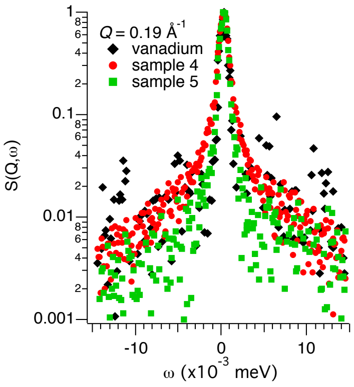


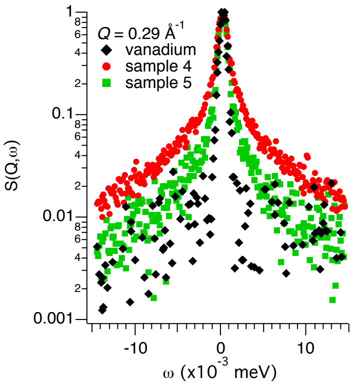


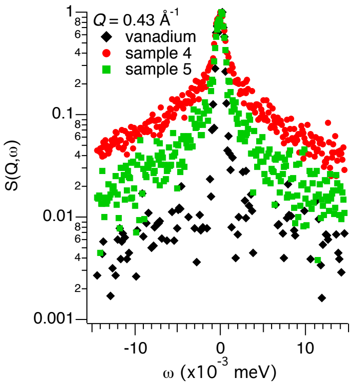


Quasielastic data

The quasielastic data were treated by the fortran program `SQW` for ILL that performs normalisation and correction for absorption. From their composition, the main contribution to the intensity for samples with deuterated water is the elastic coherent signal from the silica particles with no interference on the dynamics in the low Q regime. For light water samples (not shown), the main contribution comes from the incoherent part of hydrogenated water. For heavy water samples, a significant contribution of the dynamics comes from not only the hydrogenated ions but also from the deuterium incoherent.







In the figures above, two samples are compared to the vanadium elastic reference. In sample 4, D_2O incoherent intensity is dominant in the signal. In sample 4, the main contribution comes from the ions as seen from the slower dynamics (smaller half width), but still with a significant contribution of D_2O. The subsequent detailed analysis is then difficult since one need to take into account both the solvent and ions dynamics. The use of molecular dynamics simulation to separate the different contributions is then needed and corresponds to another part of the global project.