# Experimental Report

12/10/2014

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|---|---|---|---|
| **Proposal:** | **9-10-1316** | **Council:** | 10/2012 |
| **Title:** | Counterion correlation in colloidal solutions | | |

**This proposal is a new proposal**

**Researh Area:** Physics

**Main proposer:** **CONSTANTIN Doru**

**Experimental Team:** JUDEINSTEIN Patrick
CONSTANTIN Doru

**Local Contact:** SCHWEINS Ralf

**Samples:** Silica/SiO2
PW12O40
D2O

| Instrument | Req. Days | All. Days | From | To |
|---|---|---|---|---|
| D11 | 3 | 1 | 02/07/2013 | 03/07/2013 |

**Abstract:**

The detailed distribution of counterions close to colloidal particles (macroions) is a long-standing problem, with wide-ranging fundamental and practical implications. In particular, there is very little experimental data on the individual ion-ion interaction, although this interaction and the resulting ion correlation play an important role in biological processes. Such information could also help validate and refine certain assumptions made in theoretical and numerical studies of charged systems, e.g. in implicit solvent strategies. One often assumes that the interaction is accurately described by the DLVO model, which combines the electrostatic and van der Waals interactions, supplemented by steric repulsion. While this model has been very successful in explaining the interaction of macroscopic objects, its validity at the nanoscale is still in need of direct experimental verification.

# Report for experiment 9-10-1316 (D11)

**Proposal title**: Counterion correlation in colloidal solutions
**Dates**: 02-03 July 2013 (3 shifts)
**Participants**: Doru Constantin (main proposer), Patrick Judeinstein
**Local contact**: Ralf Schweins

## 1. Objective

The main goal of this experiment was determining the detailed distribution of counterions (**C**) close to colloidal particles (macroions, **M**). The scattered signal $I(q)$ is sensitive to the three types of interactions in the system: between macroions (**MM**), but also between counterions (**CC**) and to the cross term macroion-counterion (**MC**). We used trivalent counterions, for which the **CC** correlation is expected to play an important role.

This is a coupled SAXS/SANS investigation, and the main interest of the SANS experiment is the ability to contrast-match the counterions. As a result, the scattered intensity is only due to the macroions, interacting *via* an effective potential. The information is thus complementary to (and, hopefully, easier to interpret than) the SAXS intensity, which is sensitive to both kinds of particles.

## 2. Experiment and results

We investigated two systems: in the first one, the **M** particles are 27 nm silica spheres, while in the second one they are micelles of the P123 block copolymer (about 20 nm in diameter). In both cases, the counterions are phosphotungstic acid particles: $PW_{12}O_{40}^{3-}$ (or POMs), 1 nm in diameter. The silica system was measured at 25°C, and the P123 at 40°C. Both systems were studied over a wide range of **M** and **C** concentration, for a total of about 30 solutions. The samples were held in standard quartz cuvettes, 1 or 2 mm thick depending on the expected transmission.

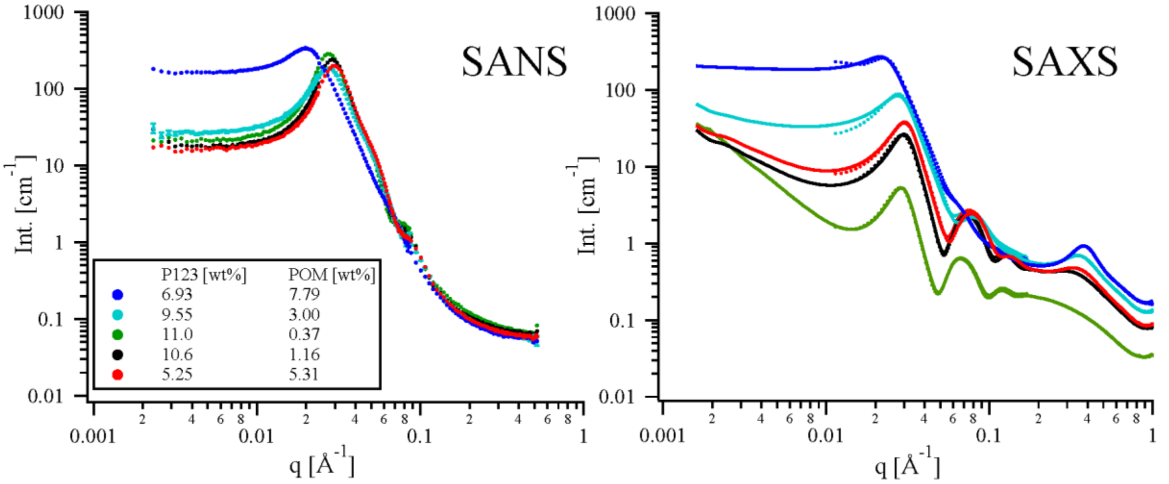

**Figure 1** : Scattered intensity $I(q)$ for a few P123 samples, in SANS (left) and SAXS (right). Note that the high-$q$ signal of the counterions, clearly visible in SAXS, is completely absent from the SANS data.

We used three experimental configurations, with sample-to-detector distances of 1.2, 8 and 28 m (at a constant wavelength $\lambda = 6$ Å), covering a scattering vector range $2.3\ 10^{-3} < q < 0.5$ Å$^{-1}$. For P123, the signal of both **M** and **C** particles is clearly visible in the SAXS data (in the low- and high-$q$ range, respectively) but only the M contribution subsists in the SANS spectra, as illustrated for selected samples in Figure 1. Unfortunately, the SLD of silica is too close to that of the POMs, so the measured signal was not exploitable.

## 3. Conclusions and perspectives

Our attempt to match out the counterions while preserving the signal of the macroions was successful for one system (P123), but not the other (silica). Fortunately, it is the former that exhibits the richest behavior (interaction peak for both the **M** and the **C** components).

Interpreting the data will require implementing an algorithm for simultaneous full-range fitting of all curves. The model structure factors will be obtained iteratively as a function of the interaction potentials between the various components. This work is in progress.

The static information will be complemented by the diffusion constants of the various species, obtained via dynamic light scattering and PFG-NMR.