Experimental report

16/09/2019

Proposal: DIR-168 **Council:** 10/2018

Title: Foam flotation for ionic metal clusters extraction and separation: measure of foam film thickness by TOFsmall angle neutron scattering

Research area:

This proposal is a resubmission of 9-10-1585

Main proposer: Olivier DIAT

Experimental team: Max HOHENSCHUTZ
Philipp SCHMID
Luc GIRARD
Alban JONCHERE
Olivier DIAT
Pierre BAUDUIN

Local contacts: Isabelle GRILLO

Samples: Sodium Hydroxide / NaOH
Surfactant Akypo(r) RO 90 VG / C38H74O12
Î±-H3PW12O40 (PW), Î±-H4SiW12O40 (SiW) salt
DCl, deuterated chloric acid

Instrument	Requested days	Allocated days	From	To
D33	3	2	01/07/2019	03/07/2019

Abstract:

/Experimental report

Proposal: EXP-DIR-168 **Council:** 2018-10

Title: Foamex

Research area: Soft condensed matter

Main proposer: Olivier DIAT

Experimental team: Max Hohenschutz
Pierre Bauduin
Philipp Schmid
Luc Girard
Alban Jonchère

Local contacts: Isabelle Grillo

Samples: BrijO10, D2O, SiW, SDS

Instrument	Requested days	Allocated days	From	To
D33	4	2+1(local contact)		2019 July 1st at 9h to 4rd at 9h00

Abstract: TOF-SANS on foam generated above a solution containing surfactants and nano-ions: inter-bubble aqueous film characterization.

Experimental Report

Foam Flotation for ionic metal clusters extraction and separation: measure of foam film thickness by TOF small angle neutron scattering.

We obtained 3 days (2 from the Directors and one from the local contact who clearly estimated that it was a minimum to get reliable data from this type of experiment) to perform for the first time TOF-SANS measurements on foam produced above a volume of an aqueous solution containing the surfactant and salts that can be extracted via a specific adsorption onto the foam films.
The non-usual objective of this proposal was to study a system containing a non-ionic surfactant to extract an ionic and "superchaotrope" species, a polyoxometalate that can interact with polar and highly hydrated surfaces or interfaces.
Measurements were performed through a 3cm diameter column with quartz windows at three different heights above a volume of solution (see figure aside).

A bit of time was used for alignment, background and normalization. Once the sample solution is poured into the column tthe foam rise due to an air flow of 5 ml/min through a sintered glass plate at the bottom of the column. The measurement protocol starts when the foam filled the first window completely carrying out 2 consecutive acquisitions per window and then several rounds of scanning the 3 windows one after the other followed by a transmission measurement at all 3 windows (in order to estimate the volume fraction of solution at each height, we found a problem to not be able to record the transmission through a semi-transparent beamstop – a modification that has to be envisaged in the future). The acquisition scan is stopped when the curves obtained through the 2nd or the 3rd windows overlapped as a function of time, indicating a stationary state of the foam. About 2h1/2 for 1 sample composition with a collection of 10-15 spectra as a function of time (between 5 and 10 mn per acquisition). It took always a bit of time to rinse the column with D2O and to refill and restart the next experiment (about 15-20 mn).
The objective of the proposal was also to work in TOF mode in order to record a spectrum over the largest q-range in one shot (0.027-4 nm^-, with both the information on micellar structure (large q) and those related to the film thickness between foam bubble (low-q), rather faceted. As explained in the proposal it is different to reproduced twice the same foam and to investigate its multi-scaled structure varying the detector position with a good overlap of the scattering curves at low and large q-vectors. The spectra were thus collected at a fixed detector distance of 7m using the two sets of detectors available in the D33 tube.

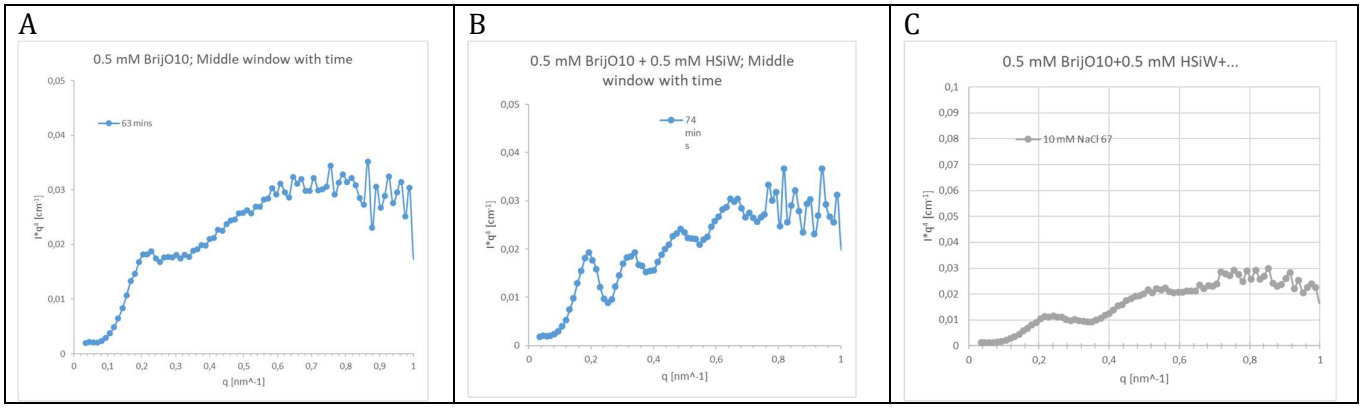
It was important to get the azimuthal averaged signal I(q) as acquisitions are collected to evaluate the evolution of the scattered signal and see how to adjust the flotation parameter in case of problem. We have lost a bit some time due some crashes of the TOF analysis program (unfortunately always during the nights as usual on large facilities!) and also had some computing problem of background subtraction which caused some misalignments between scattering curves from both sets of detector – background subtraction between both detectors. This was determinant to evaluate if we had to redo the experiment with the same sample of to go to the next.
It was important to note that the scattering of the foam at large angle was approximatively equivalent of those obtained with the same sample in 1mm quartz cell and at the same condition of sample to detector distance when using monochromatic mode.

However, we obtained some very interesting results that we are analyzing for publishing. To summarize, see below 3 sets of curves plotted in q^4I vs q because of the main q^{-4} decay of the recorded signal relative to the Frenel's reflectivity law at low q (and above a critical q-vector of about $1.8\ 10^{-2}\ A^{-1}$, taking into account the SLD of D2O vs air) and to highlight the Porod regime of the micellar aggregates in suspension within mainly in the Plateau border, detectable at larger q. These spectra shown here, were obtained at the middle position of the column and after 1 hour of foaming. When oscillation are observed at low q, this is due to interferences between part of the beam which is refracted and reflected on the second diopter of the film. Thus, in the Fourier space this results in oscillations with a period Δq related to the thickness of

the film with the relationship $T = 2\pi/\Delta q$. When no oscillation is observed and the signal decreases in a quasi q^{-4} power law, this means that the distance between two films is too large and that the foam is rather wet. For foams with a large number of reflecting surfaces (films), scattering rings are observed on the 2D detector. On the contrary, for foams with less film and so rather dry, with large-size bubbles, radial scattering spikes are observed.

The first *A* scattering curve is a signature of a thin film (we know also by visual observation that the foam is facetted). Unfortunately, the second oscillation is not visible due to a strong signal from the micelles present within the foam, within the Plateau border and within the bubble film (we worked at 10 times above the CMC of the Brij-O10). As soon as a superchaotropic salt is introduced in the solution, POM SiW here, large oscillations appear with higher frequencies (curve *B*) characteristics of the presence of thicker films within the foam but very well correlated due to a much stronger interaction that exists between the facing interfaces. This is due to electrostatic repulsion induced by the adsorption of the superchaotropic anions onto the surfactant films. Then, in a third step, when a more classical NaCl salt is introduced in the solution, 10mM for this example, a clear screening of the ionic interactions is detectable inducing a decrease of the film thickness of about a factor 3.

So first an electrostatic repulsion within a foam is quantified through a non-electrostatic interaction between the nano-ions and the surfactant and then a screening effect can be tuned adding some brine.



As mentioned before, due to the lack of an online transmission data, it was not possible to quantify the volume fraction of solution within the foam and at the different heights of the data collection although this would have been important in order to evaluate the local drainage and thus the stability of the foam.

Nevertheless, at the inverse of the AKYPO foaming system at pH above the Akypo's pKa and in interaction with multivalent ions such as Nd^{3+} [Micheau et al, Langmuir 2013] we know from laboratory experiments that a stronger drainage is observed in the first case compared to the second case. This is certainly due to a much less cohesive film monolayer when the film is nonionic. So, the extraction of ions via foam flotation can be considered as less favorable when nano-ions alone are present. However, in presence of other salt, the foam is again slightly drier reducing a water transport within the foam, at the profit of the ion concentration expected via this process. So, the optimal ratio nano-ion/background salt has to be determined to get the higher extraction/concentration efficiency. These comments are coherent with what we observed via TOF-SANS but have to be confirmed by investigating free drainage at different column heights.

In supplement, we varied the surfactant concentration for a fixed SiW concentration and we varied the POM concentration for a surfactant concentration. We found an optimal ratio (saturation of adsorption and ion screening effect) that we will have to check further, varying the nano-ion charge. We have also tried to use na ionic surfactant (SDS) at the same ionic molar ratio than with nano-ion and similar reasoning was made. We observed also a kinetics in the micellar concentration variation that appears to be different from timescale to achieve the stationary state in term of inter-bubble thickness: A point that has to be investigate in the future.