EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **The modification of the water network by hydrostatic pressure and cosolvents near the liquid solid interface**	**Experiment number**: SC-3600
Beamline: ID15A	**Date of experiment**: from: 05/06/13 to: 11/06/13	**Date of report**: 24/09/2013
Shifts: 18	**Local contact(s)**: Dr. Veijo Honkimäki	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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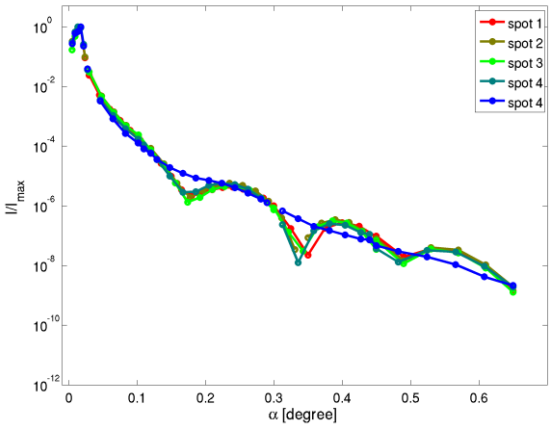
Report:

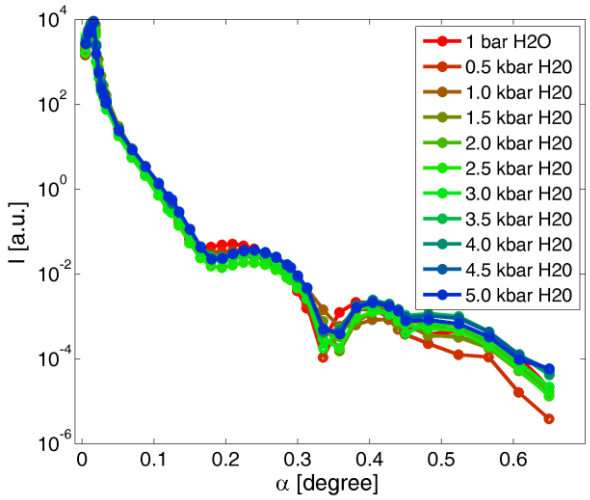
The exact structure of the solid-liquid interface was studied for many years now. Special interest was attracted by hydrophobic solid surfaces. The existence of an electron depleted region next to the interface, the so-called hydrophobic gap, was controversially discussed both in experiments and MD simulations. Many experimental high resolution studies revealed the existence of this layer possessing a low electron density compared to water. However, this very thin layer is often hidden by low resolution as a consequence of the restricted access to the *q*-space in experiments. In the existing studies of the hydrophobic gap, mainly the effect of substrates with different hydrophobicity was studied. Only little is known about the role of the water structure close to the solid-liquid interface. Thus, we studied the solid-liquid interface with x-ray reflectivity (XRR) while varying the water structure by applying high hydrostatic pressure (HHP) up to 5 kbar and by addition of the water network stabilizing agent trimethylamine-N-oxide (TMAO).
Studies on bulk liquid water show that elevated pressure causes changes in the local water structure indicated by smaller oxygen-oxygen distances but also by an increased coordination number. This effect was explained by a closer packing within the first coordination shell. In the past years, TMAO was widely studied for its interesting properties as a water network stabilizer.

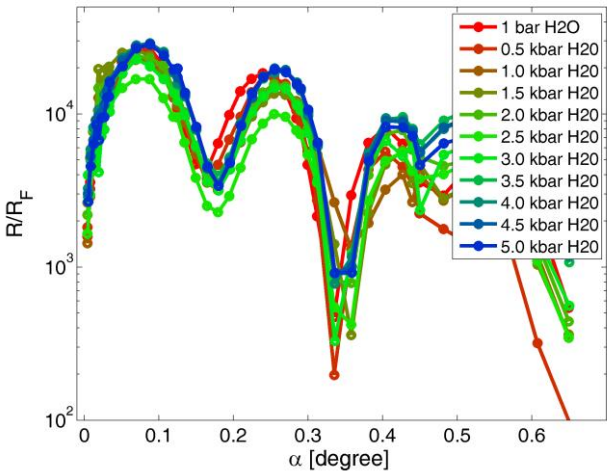
The HHP-XRR experiments were performed at ID15A, using a photon energy of 70 keV and a beam height of 5 µm. As hydrophobic substrate, we used silicon wafers with a size of 8 x 8 mm that were covered with a monolayer of octadecyl-trichlorosilane (OTS). Experiments were performed in a custom made sample cell that can sustain high hydrostatic pressures up to 5 kbar. The installation of this cell at ID15A was without any difficulties.



To avoid beam damage of the OTS layer, the sample was shifted horizontally after each reflectivity curve. Thus, we checked first the homogeneity of our samples. The Figure on the left shows reflectivity curves from 4 different spots on an OTS-coated silicon wafer immerged in water. From this figure, it can be seen that the sample is homogeneous and that the OTS layer is destroyed if a second reflectivity is measured on the same spot.

In a first series of experiments, we investigated the interface between the hydrophobic OTS wafer and ultrapure water at room temperature and increasing pressure. The left panel of the Figure below shows the reflected intensity as a function of the incident angle. A slight variation in the reflectivity curve is observed as the pressure is increased from ambient pressure to a pressure of 5 kbar. The right side shows the same data divided by the Fresnel reflectivity to highlight small changes. However, the variation is very subtle and it seems on the first sight that high hydrostatic pressure does not considerably modify the structure of the hydrophobic solid/liquid interface.





The Figure below displays the experimental results that were measured at the interface between OTS and a 1 M TMAO solution. (Left panel: reflectivity; right panel: divided by the Fresnel reflectivity). Concentrating on the shape of the curve around the second maximum, it is visible that a pronounced dip appears with increasing pressure. A more detailed analysis will elucidate if this modification is caused by an accumulation of TMAO molecules at the interface or can be attributed to a modification of the hydrophobic gap.