EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Kinetics of water imbibition at a silicon direct bonding interface	**Experiment number**: 32-02 782
Beamline: BM32	**Date of experiment**: from: 7/12/2016 to: 14/12/2016	**Date of report**:
Shifts:	**Local contact(s)**: Francois RIEUTORD and Samuel TARDIF	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

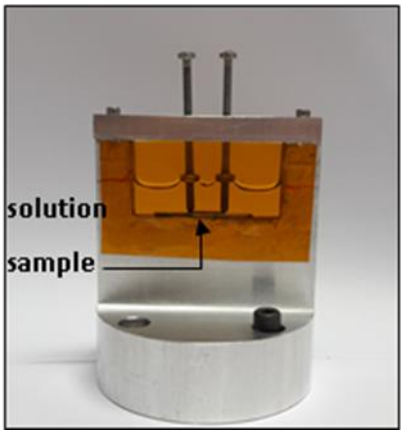
The objective of this experiment was to determine the ion distribution profile from surfaces of grafted layers of alkoxysilanes, having various functional headgroups (amino and mercapto) in electrolyte solutions containing ions having more or less kosmotrope character using hard X-Ray Reflectivity.

Sample preparation

Self-Assembled monolayers were made by supercritical CO_2 grafting on silicon substrates previously activated by nitric acid 10% wt. Organic molecules grafted on the surface were 3-(mercaptopropyl)trimethoxysilane (MPTMS) with a mercapto group and N-(3-(trimethoxysilyl)propyl)ethylenediamine (AEAPTMS) with an amino group. Non-grafted samples used as a reference were called HNO_3. Electrolytic solutions used for the measurements were XCl_y with X= Cs, Ba, Ca, Mg, Sr, La and $1 < y < 3$.

Hard X-Ray reflectivity measurements

All the samples were cut with the dimensions 0.5 x 1.0 cm and fixed in a specific cell (Figure 1). The cell was filled with DI water or an electrolyte solution. Measurements were performed from $-0.2 < \theta < 3$. Scans were taken every 10 minutes until there were no more visible changes between reflectivity curves.

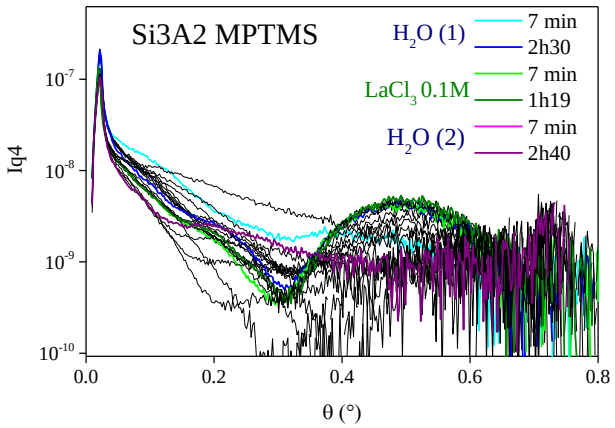


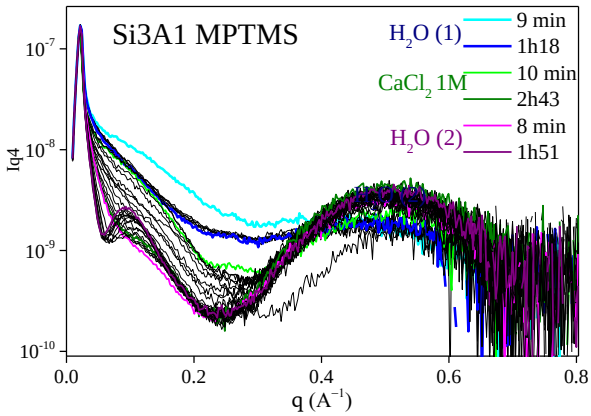
1) Adsorption and desorption of ions on grafted and non grafted silica thin films

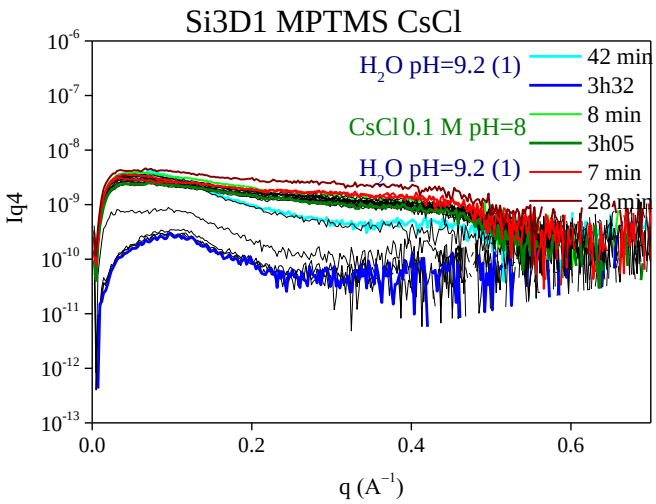
Experimental

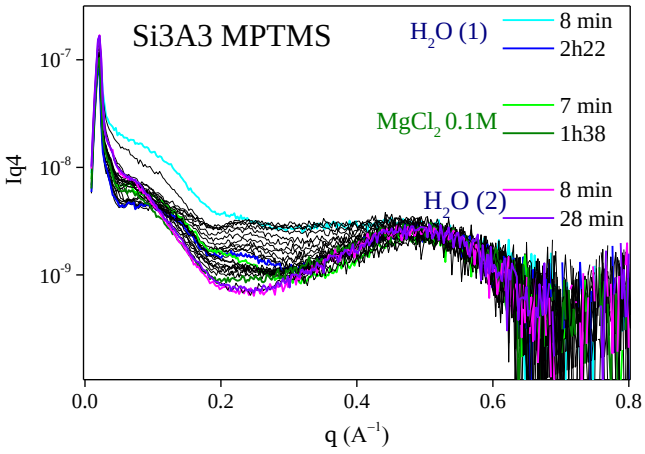
- The cell was firstly filled with DI water
- Water was removed from the cell and an electrolyte solution was poured with a syringe.
- XRR reflectivity curves were recorded in order to study the kinetics of ion sorption on the surface of the sample
- Electrolyte solution was removed and the cell was filled of water to have informations about the desorption kinetics of ions.

Results







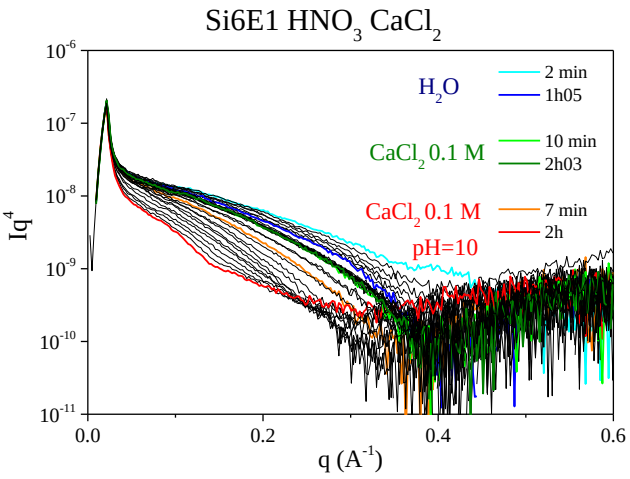


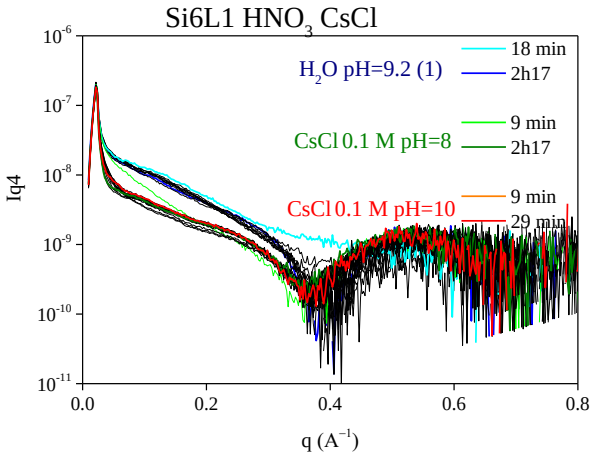
2) Influence of pH on the ions adsorption-desorption on grafted and non grafted silica thin films

Experimental

Measurements were done using the same protocol that 1) but with DI water and electrolyte solutions at pH=9. Desorption was not studied in this part.

Results





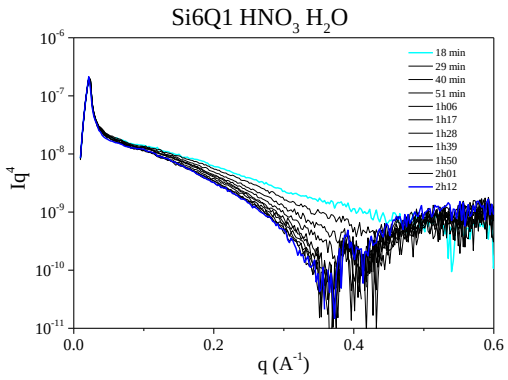
3) Influence of the presence of water before electrolyte measurements in grafted and non grafted silica thin films

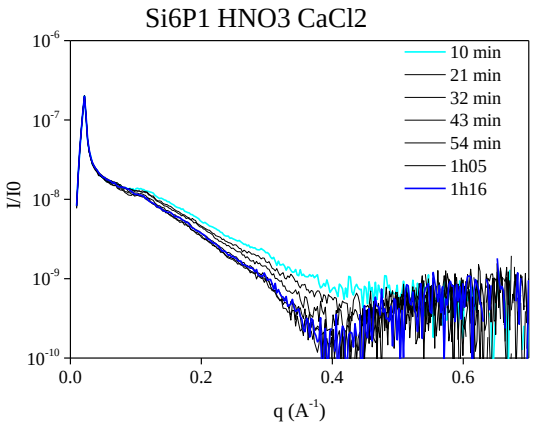
Experimental

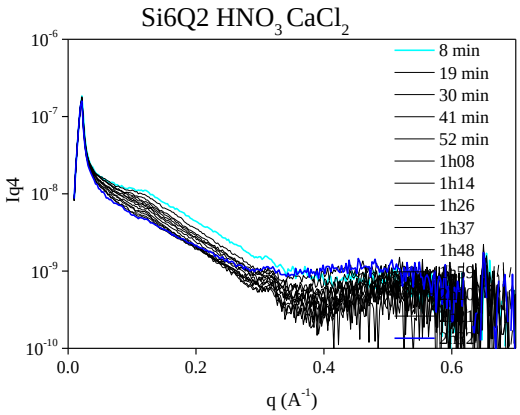
- The cell was filled directly with electrolyte solution. XRR measurements were taken until stability of the reflectivity curves.

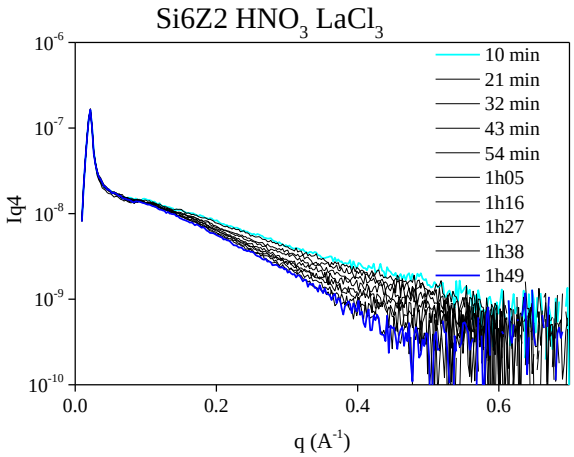
Results

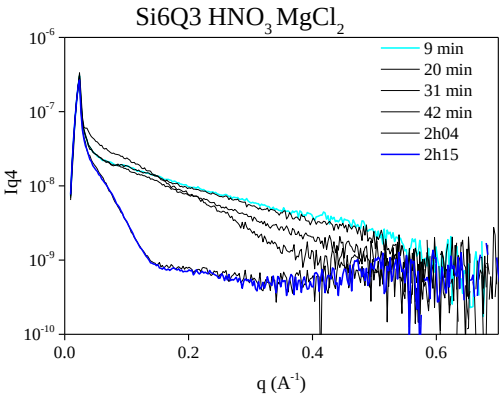
- HNO_3 activation

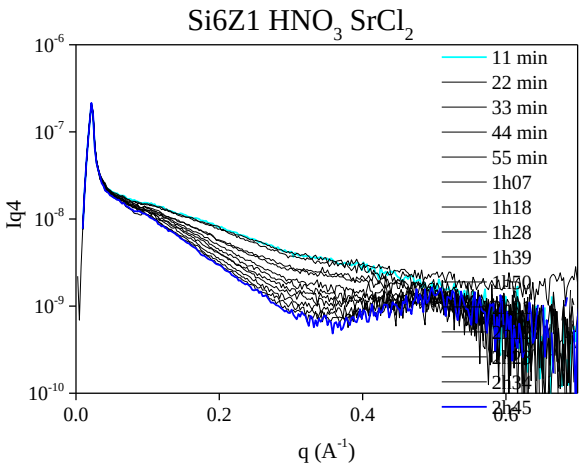


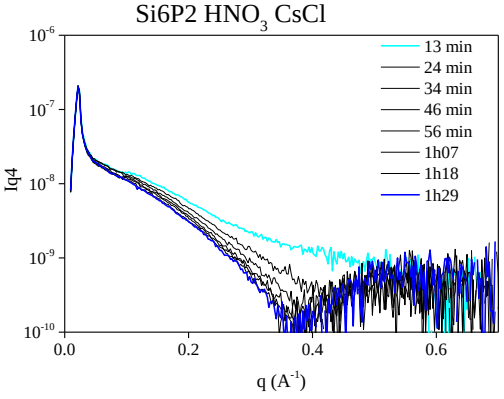




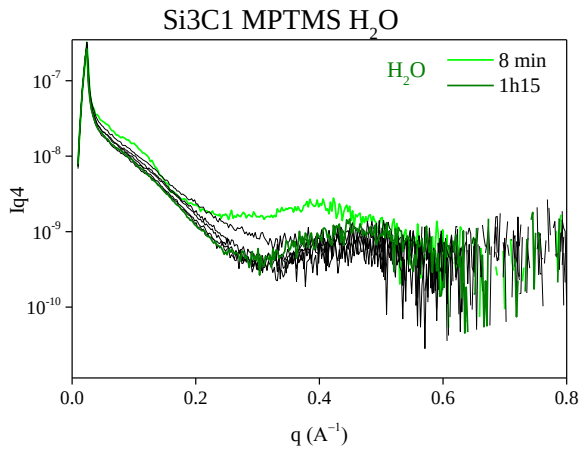


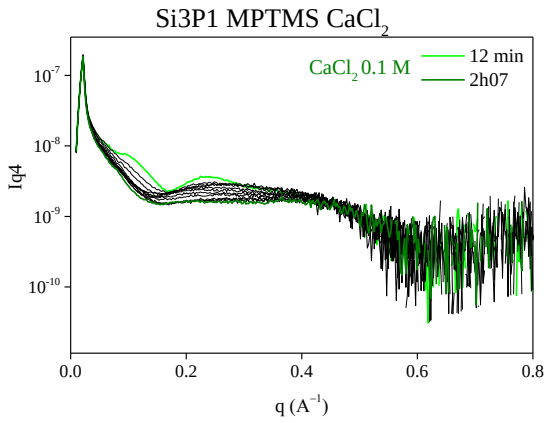


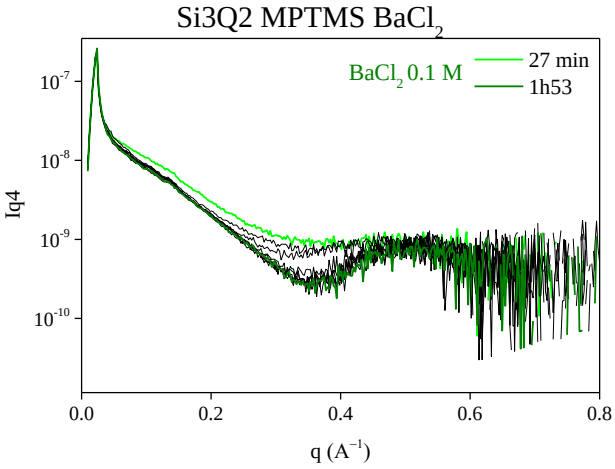


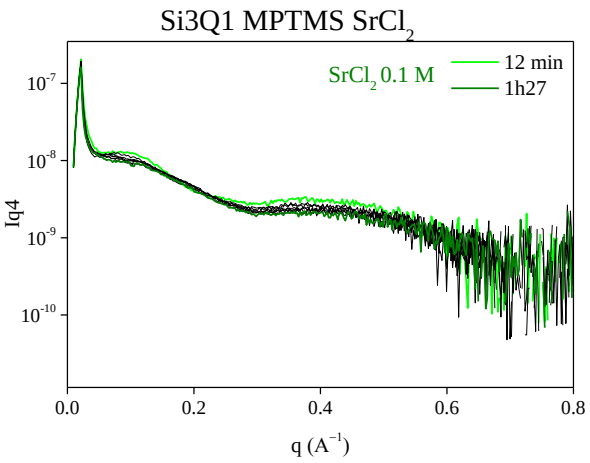


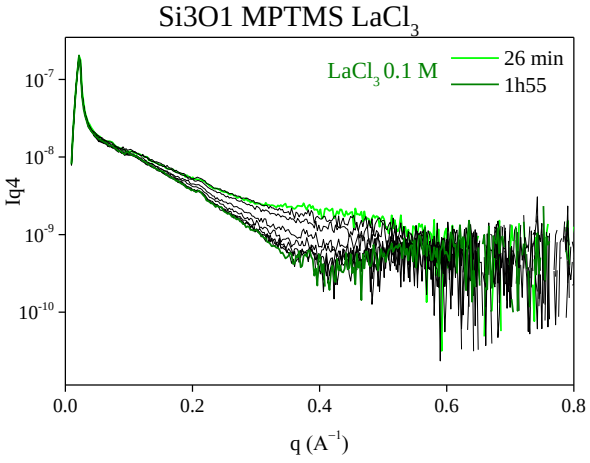
- MPTMS grafting

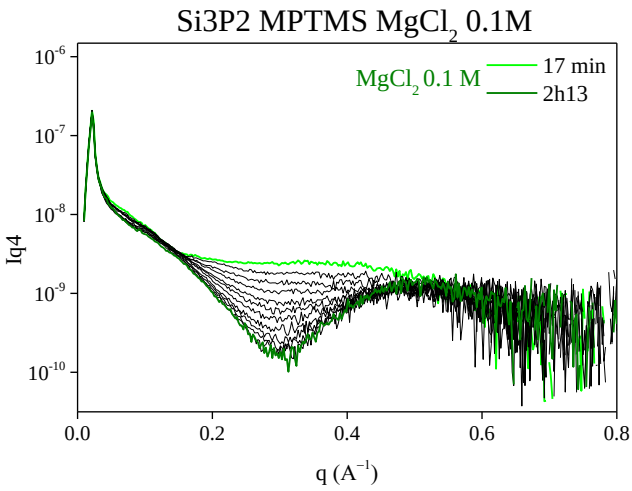




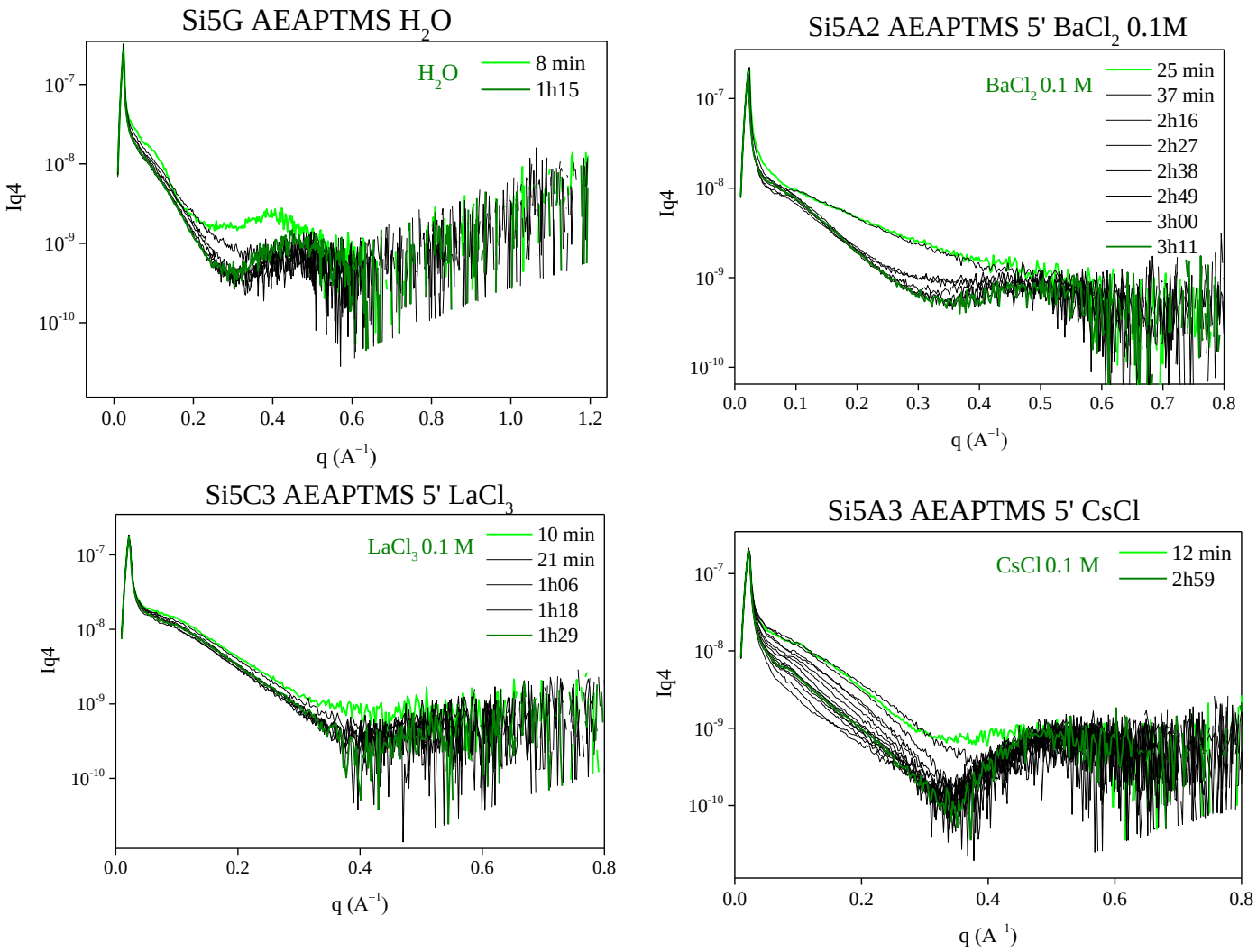








AEAPTMS grafting



Conclusion

Reflectivity curves show differences over time depending on the electrolyte. The non-grafted samples show changes with most of the ionic species. In MPTMS grafted samples, the variations are visible in $BaCl_2$, $MgCl_2$ and $LaCl_3$, while in $SrCl_2$ the reflectivity remains quite stable. For the AEAPTMS grafted samples, differences between the reflectivity curves are visible in $BaCl_2$ and CsCl. The decrease of the density may come from the increase of the layer roughness and may be directly connected to the formation a diffuse layer.

Effects of the pH

In the case of $CaCl_2$, differences are observed with the pH. For CsCl the differences are less evident.

[1] M.J. Bedzyk, G.M. Bommarito, M. Caffrey, T.L. Penner, Science, 248 (1990) 52–56.