



## Experiment Report Form



	<p><b>Experiment title:</b> Impact of the size of the nanoconfinement on the ions distribution at the silica / solution interface</p>	<p><b>Experiment number:</b> 32-02 811</p>
<p><b>Beamline:</b> BM32</p>	<p><b>Date of experiment:</b> from: 26/04/2018 to: 02/05/2018</p>	<p><b>Date of report:</b> 04/05/2018</p>
<p><b>Shifts:</b></p>	<p><b>Local contact(s):</b> Francois RIEUTORD and Samuel TARDIF</p>	<p><i>Received at ESRF:</i></p>
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## Report:

The objective of this experiment was to determine the impact of the confinement size and the pH on the sorption kinetics of various electrolyte solutions on parallel plane silica surfaces spaced of few nanometer (nanochannels 2 and 4 nm) using hard X-Ray reflectivity (27 keV). For this purpose we used several salt solutions  $XCl_2$  ( $X = Ba^{2+}, Ca^{2+}, Mg^{2+}$ ) at different concentrations (0.2 – 1 M) and pH values (pH 2 and 8) in order to investigate the influence of ions having more or less kosmotropic property. From the electron density profiles obtained, the filling kinetics of these nanochannels and the validity of conceptual models used to describe the diffusive layer can be studied. Moreover, the experimental results will be compared to the results obtain by atomistic modelling.

### Sample preparation

Nanochannels (2 and 4 nm) were dried in a vacuum oven at 200 °C for 3 days in order to determine the electron density profile of the dried samples. Subsequently the nanochannels were immersed in electrolyte solution  $XCl_2$  ( $X = Ba^{2+}, Ca^{2+}, Mg^{2+}$ ) at different concentrations (0.2 – 1 M) and different pH values (pH 2 and 8) and the X-Ray reflectivity was measured after different times and at several distances from the edge to get information about the filling kinetics.

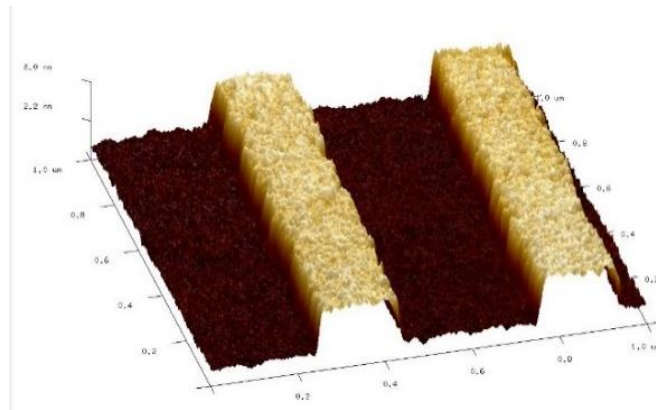


Figure 1: The AFM image shows the well-defined channels in this experiments having a height of 2 and 4 nm.

### Hard X-Ray reflectivity measurements

All the samples were fixed in a specific cell (Figure 2) and measured in dried state. Subsequently the cell was filled with the appropriated salt solutions. Regarding the long term experiments the nanochannels were immersed in 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.

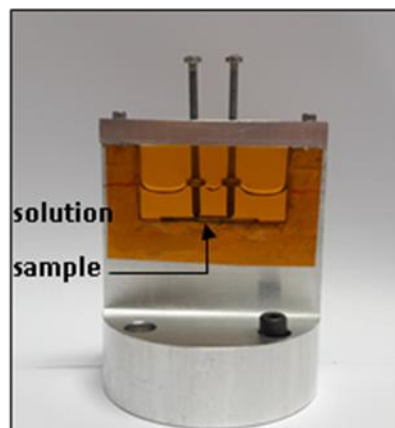


Figure 2: Cell used for X-Ray Reflectivity measurements. The nanochannels were fixed using two screws and filled with the appropriate electrolyte solutions.

## Results

The nanochannels were measured in a dried state and afterwards filled with water and electrolyte solution. Since beam time was the consecution of a previous experiment, we show the long-term kinetics of nanochannels-filling during 8 months in solution having two different concentrations (0.2 and 1 M) and at neutral pH. Furthermore, we studied the impact of the pH on the filling kinetics. The following graphs (Figure 3 - 6) highlight the reflectivity data as a function of the channel size and at two different pH values. The pH dependent measurements were performed during 8 days of immersion in 1 M solutions.  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions were only measured at a neutral solution pH and pH at 8.

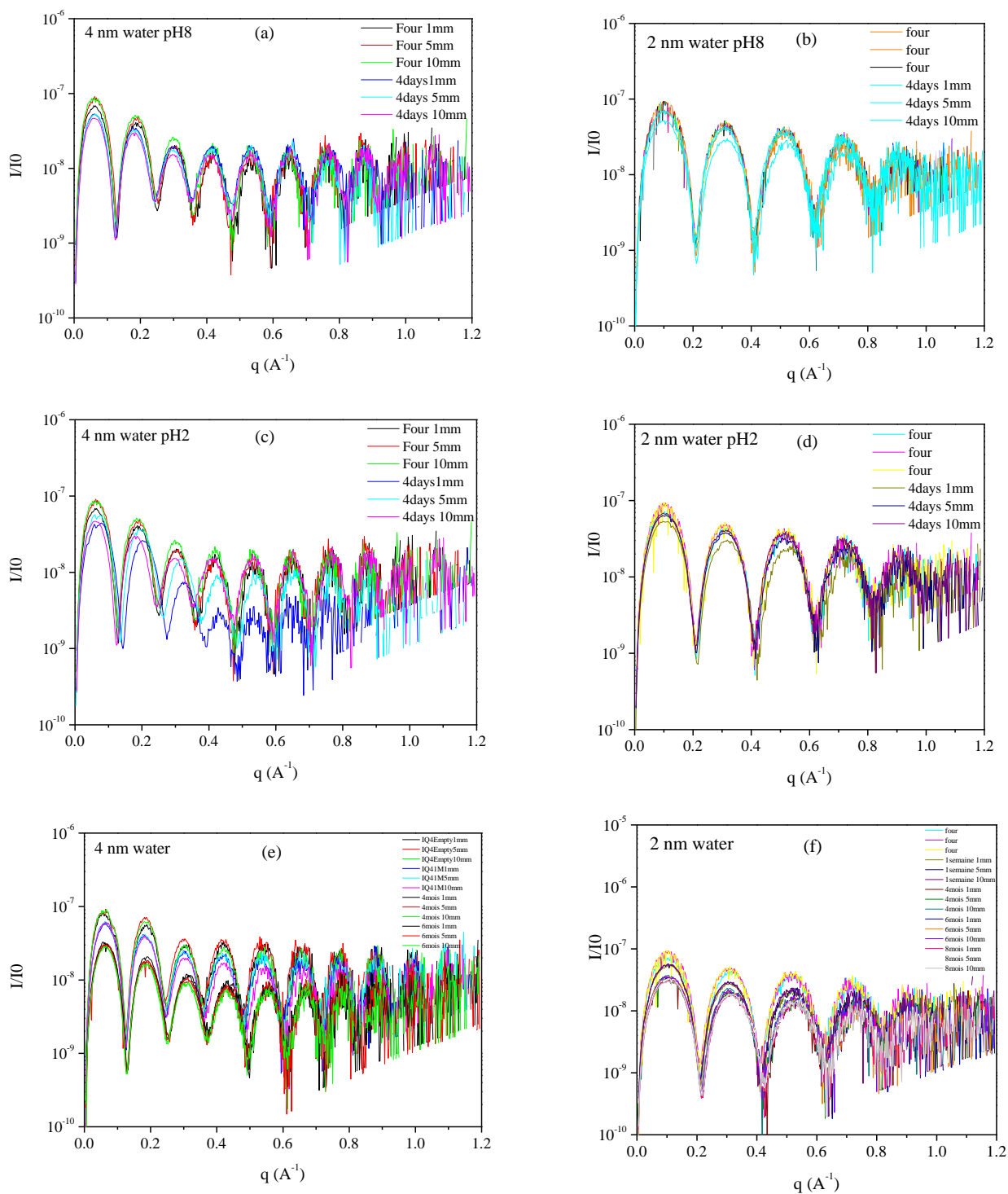


Figure 3: X-Ray Reflectivity curves obtained for water in different sizes of nanochannels (2 and 4 nm). Filling kinetics at pH 2 and 8 were performed during 8 days (a –d) and at neutral pH during 8 months (e, f).

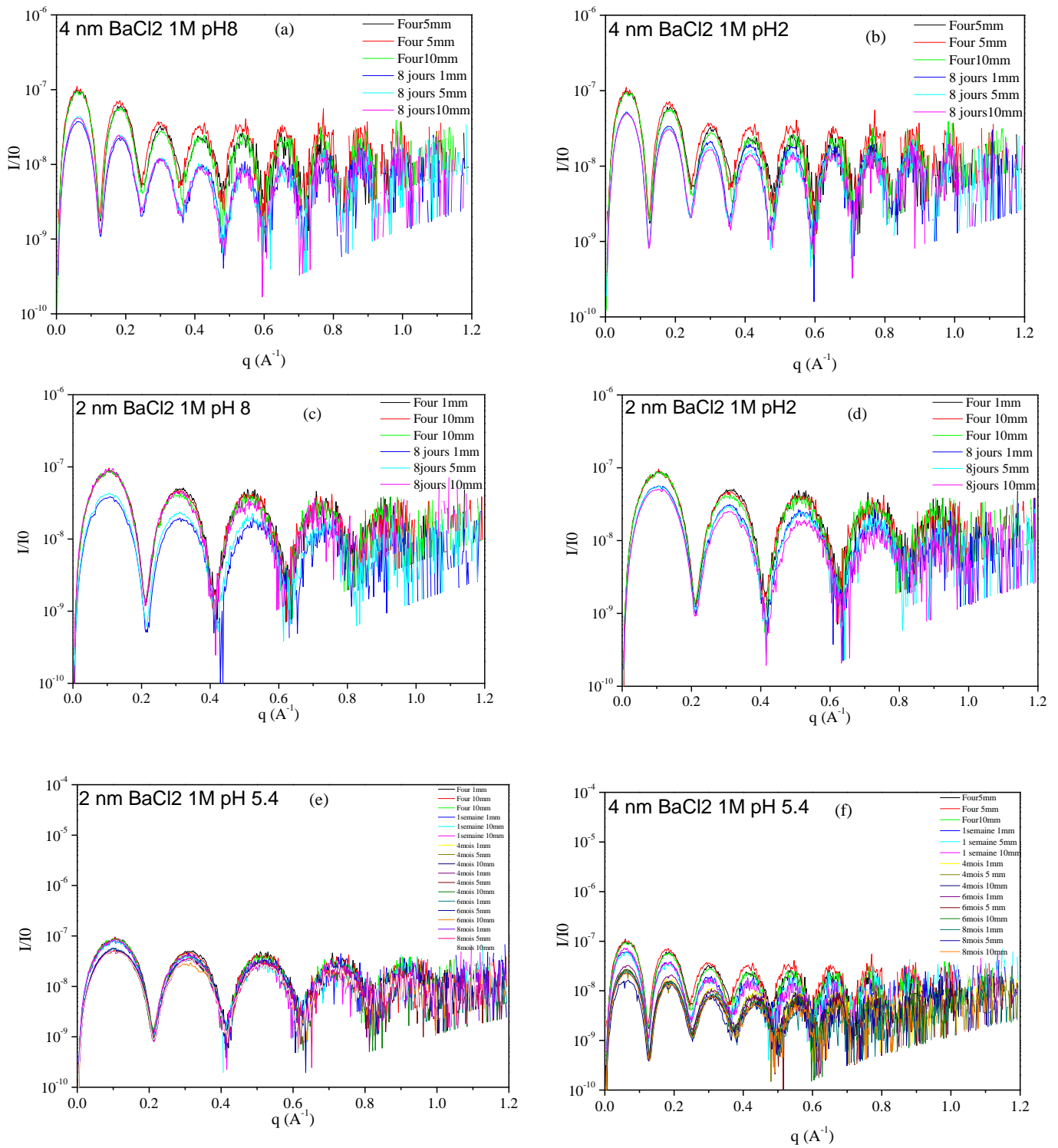


Figure 4: X-Ray Reflectivity curves obtained for  $\text{BaCl}_2$  at 1 M at pH 8 and 2 (a-d) in different nanochannel sizes (2 and 4 nm) and at neutral pH during 8 months (e, f).

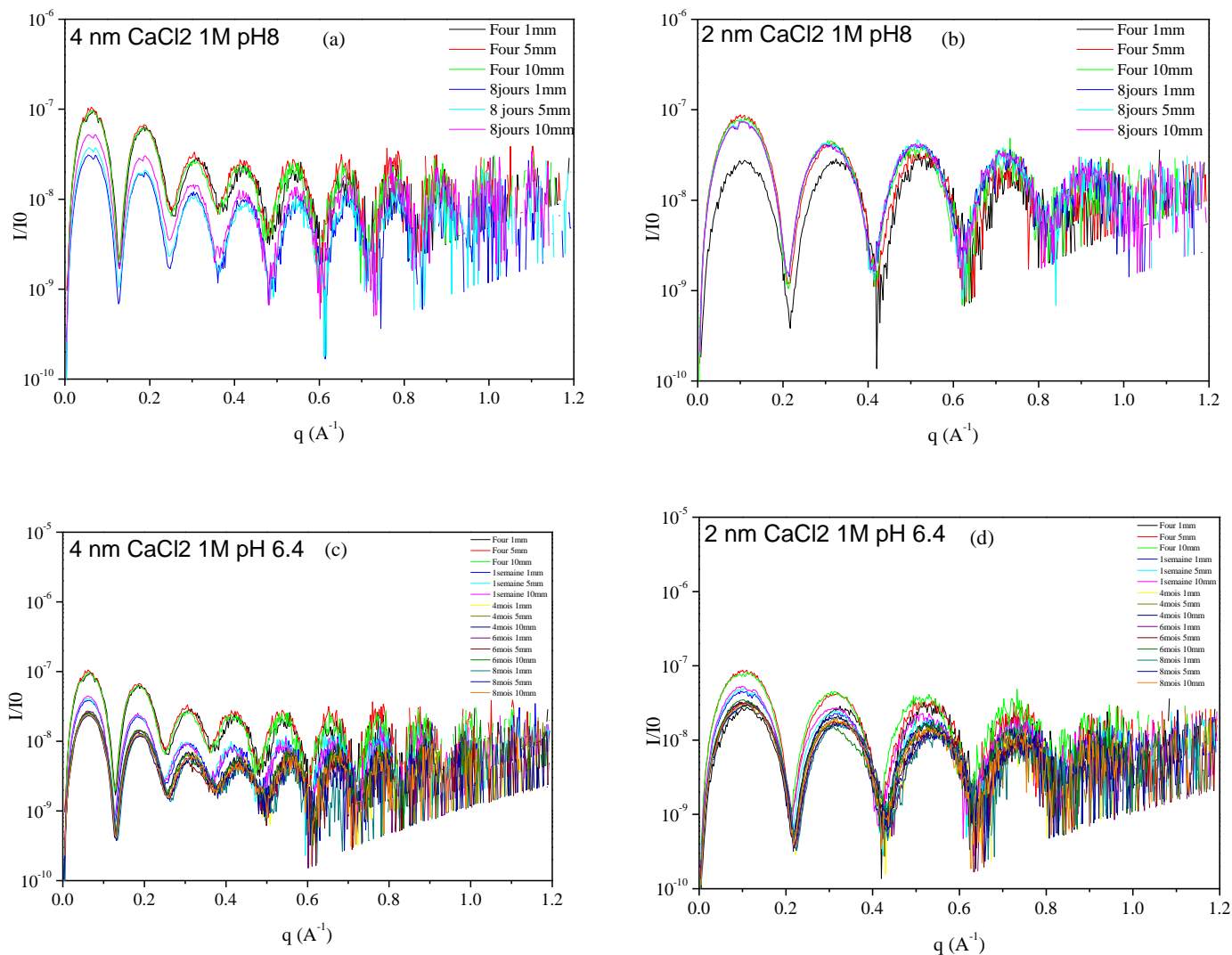


Figure 5: X-Ray Reflectivity curves obtained for  $\text{CaCl}_2$  at 1 M at pH 8 (a, b) in different nanochannel sizes (2 and 4 nm) and at neutral pH during 8 months (c, d).

Concerning the long-term filling kinetics of  $\text{BaCl}_2$  in 2 nm nanochannels, we observed that there is almost no evolution of the reflectivity curves after 8 months. However, for  $\text{BaCl}_2$  in 4 nm nanochannels an evolution was detected corresponding to a continuing filling of the channels. The pH dependent measurements revealed that there is indeed an impact of the pH on the filling kinetics. Assuming more deprotonated silanol groups at the nanochannels surface for pH8, the filling is accelerated compared to pH2. The same results were found for  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions except for the 2 nm nanochannels. The reflectivity within the 2 nm channels decreased after 8 months indicating that the filling process is still not finished. The differences can be explained by the different ion radii.

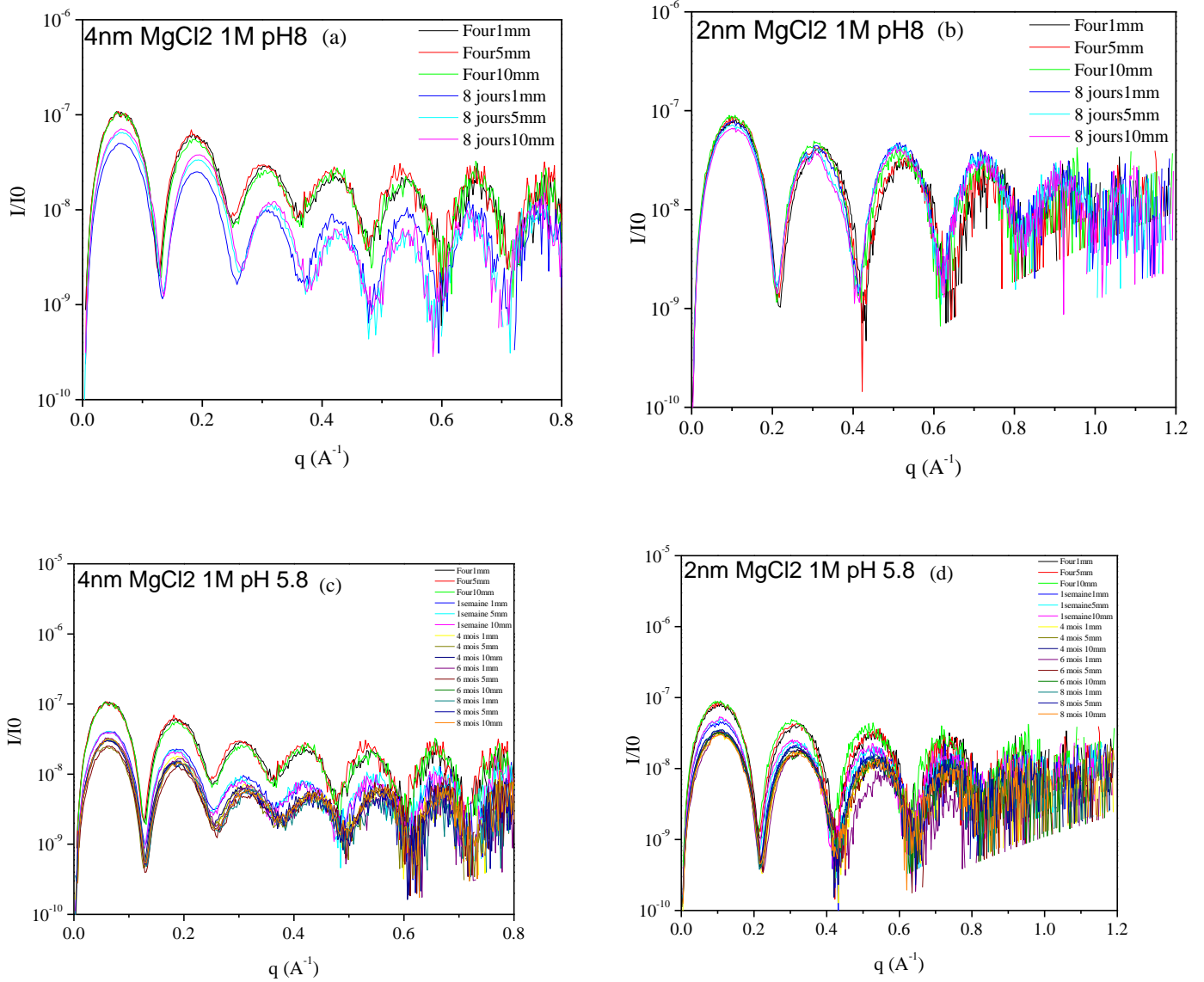


Figure 6: X-Ray Reflectivity curves obtained for MgCl<sub>2</sub> at 1 M at pH 8 (a, b) in different nanochannel sizes (2 and 4 nm) and at neutral pH during 8 months (c, d).

## Conclusion

Generally, reflectivity measurements during the filling of nanochannels with various electrolyte solutions at different concentrations and pH values revealed that the filling kinetics are dependent on several parameters. Regarding our short-term kinetics at different pH values, we observed an accelerated filling at higher pH values. Moreover, the filling of 4 nm nanochannels is faster than for 2 nm. The time required to fill the channels is longer for Ba than for Ca and Mg. Eventually, it would be interesting to analyze the pH dependent samples at a long-term in order to emphasize the pH dependent kinetics.