

# Confined Electrolytes at the Nanoscale: an X-ray Reflectivity Study

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When a liquid is confined within a nanometer-sized gap, interfacial and size effects confer to the system properties different from those observed in bulk fluids [1]. For electrolytes one expects that confinement influences the hydration of cations near the confining walls, in our study muscovite mica surfaces. Knowledge of the ordering behavior of the electrolyte's hydration shells under confinement contributes to our understanding of, e.g., friction, and diffusion and corrosion phenomena in Nature and technology. .

We have adapted a surface force apparatus (SFA) [2] to be used as confinement device in an X-ray reflectivity (XRR) experiment conducted at cSAXS (XSA12) beamline of the Swiss Light Source at PSI. Two cylinder-shaped muscovite mica membranes were made to approach each other and a flat contact area was formed in which droplets of RbCl, CsCl and BaCl<sub>2</sub> solutions at different concentrations were confined.

To achieve such confinement, we had to screen out the double layer repulsion and allow attraction between the mica membranes, working at concentrations with the Debye length  $\lambda_D < 1$  nm.

We have performed XRR experiments from the contact area as a function of the momentum transfer  $q$  ranging from 0 to 7 Å<sup>-1</sup>. Model dependent fits to the measured reflectivity  $I(q)$  [3] allowed us to determine the minimum gap distance (1.84 nm for RbCl, 1.64 nm for CsCl and 3.21 nm for BaCl<sub>2</sub>) and the electron density profile along the confinement direction [4]. The profiles indicate an ordered layering of the liquid within the gap, with the layering being most pronounced for hydrated ions closest to the confining walls. A comparison between the structures of confined chlorides with different monovalent and divalent cations (Cs<sup>+</sup>, Rb<sup>+</sup> and Ba<sup>2+</sup>) at different concentrations reveals ion specific features that can be related to ion size, valence and hydration energy.

## References

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**Primary author:** LIUZZI, Simone (Paul Scherrer Institut)

**Co-authors:** VAN DER VEEN, Johannes Friso (Paul Scherrer Institut); Prof. HEUBERGER, Manfred (EMPA, 9014 St. Gallen, Switzerland); Dr GUIZAR-SICAIROS, Manuel (Paul Scherrer Institut); Dr ESPINOSA MARZAL, Rosa M (ETH Zurich, 8093 Zurich, Switzerland); Mr CHODANKAR, Shirish (Paul Scherrer Institut)

**Presenter:** LIUZZI, Simone (Paul Scherrer Institut)

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