

Experiment SC 2566 was carried out on beamline ID10B between May 13 and May 19 2009. The aim of this experiment was to assess the influence of ion specificity on the ion concentration profiles at the mercury/aqueous solution interface, as analyzed by the evolution of reflectivity. In a first step, the feasibility of the technique applied on mercury surface was addressed upon measuring reflectivity of unpolarized mercury (of which the surface potential lies then at the so called Open Circuit Potential OCP) in water and various monovalent salts at a concentration of 0.1M. The concentration of some salts and to a lesser extent the applied potential was modified. Table 1 presents the successfully carried out experiments.

Salt	Bulk concentration	Applied potential (with respect to calomel reference electrode)
NaCl	1M	OCP
NaCl	1M	"-1,0V
NaCl	1M	"-0.6V
NaCl	1M	"-0.4V
Water		OCP
LiCl	1M	OCP
LiCl	1M	"-0.6V
LiCl	1M	"-1,0V
NaCl	0,1M	OCP
NaCl	0,1M	"-0.6V
NaCl	0,1M	"-1,0V
NaBr	0,1M	OCP
LiCl	0,1M	OCP
LiCl	0,1M	"-0.6V
LiCl	0,1M	"-1,0V
KCl	0,1M	OCP

Table 1 : Summary of the exploitable experiments carried out at ID 10B.

The data depicted in Figure 1 were easily obtained without making large effort for finding the interface before data acquisition (unlike eg other systems such as oil/water interface). They clearly reveal an influence of the nature of both anions and cations on reflectivity measurements. Unfortunately, due to the energy available on ID 10B (22 keV) heavier ions such as Rb or Cs could not be tested as they absorb X-rays to a very large extent. For instance, a 1M NaBr solution had a transmission of 0.

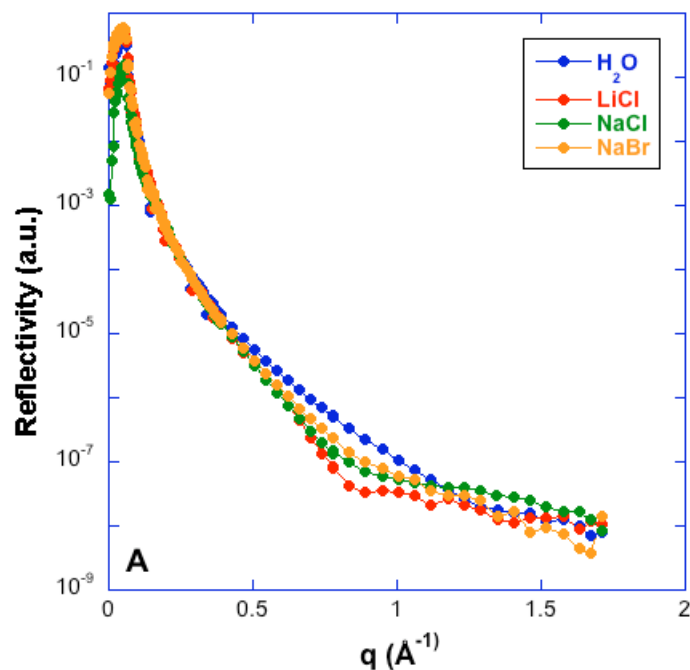


Figure 1: Evolution of reflectivity at the mercury/aqueous solution interface for various salts at a concentration of 0.1M/L

Given this, we performed additional experiments varying the concentration of NaCl and LiCl. As qualitatively expected, a decrease of the reflectivity with increasing bulk concentration was obtained (Figure 2).

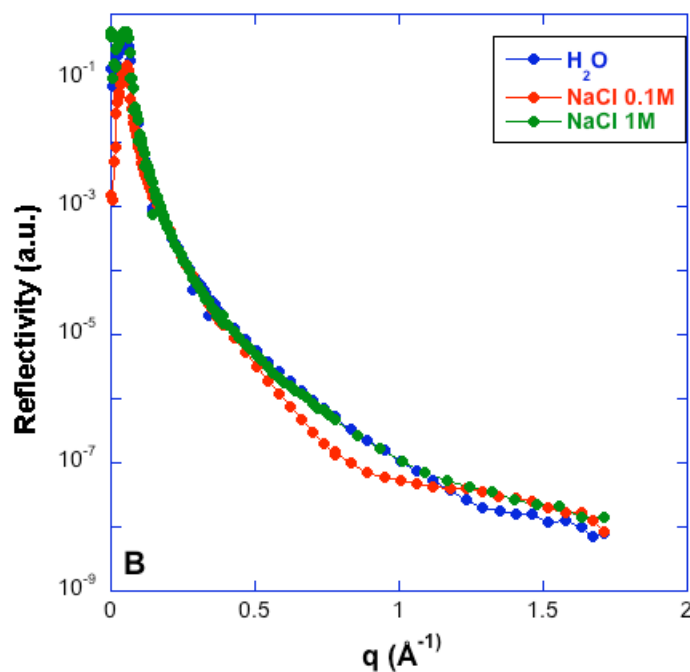


Figure 2: Evolution of reflectivity at the mercury/aqueous solution interface for NaCl at various concentrations.

Finally, we also explored the influence of applied potential on ion specificity at (polarized) mercury surface. As shown in Figure 3, electrostatics strongly impact reflectivity measurements. Unfortunately, the range of potentials investigated was limited due to undesired electrochemical reactions occurring at the stainless steel used as a building material for the reflectivity cell, and some of the curves obtained under such conditions were clearly unexploitable. Future experiments will then be performed in cells with design that minimizes such disturbing effects and enhances safety manipulations.

Quantitative modelling of these data is currently in progress, in order to establish the concentration profiles in the very close vicinity of the surface (1-3 nm) as a function of ion nature, bulk concentration and applied potential.

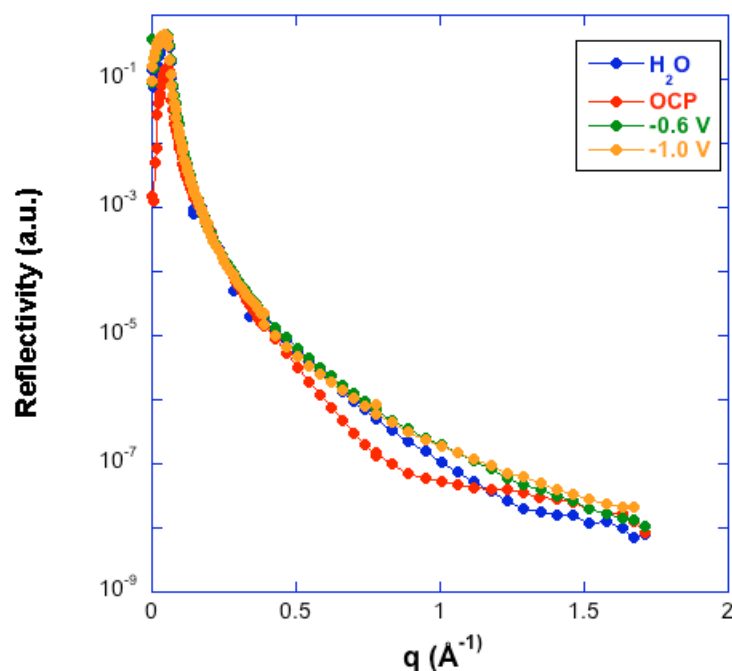


Figure 3: Evolution of reflectivity at the mercury/aqueous solution interface for NaCl at various applied potentials.