

# Probing distribution of Br<sup>-</sup> ions in the CTAB monolayer using resonant X-ray reflectivity

Kamil Wojciechowski, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland  
Thomas Gutberlet, Jülich Centre for Neutron Science, c/o TU Munich, Lichtenbergstr. 1, D-85747 Garching, Germany

Tetraalkylammonium salts are major components of anion-selective membranes of Ion Selective Electrodes (ISEs). The analytical signal of ISEs is generated through the charge separation at the interface between the ion selective membrane and the test solution. However, the exact mechanism of ion partitioning and charge separation across the interface is not yet known. Due to a significant surface activity of tetraalkylammonium salts used in ISEs, an interfacial mechanism seems to be the most probable way to explain the response of ISE.

In the present experiments we have made first attempts to highlight the interfacial concentration of bromide anions at air-water and organic-water interfaces in the presence of the model tetraalkylammonium salt, cetyltrimethylammonium bromide (CTAB) by resonant x-ray reflectivity. The water-air and organic-water interfaces serve as models of the membrane-aqueous phase interface in ISEs. The adsorption of CTAB salt at different interfaces has been intensively studied, but not in the framework of the electrical response of ISEs. Especially, no element-specific information is available so far for CTAB. Our aim was to study the concentration profile of bromide ions as counterions in the Gibbs monolayer of CTAB at this water-air and water-organic interface.

Measurements were performed under both resonant and non-resonant conditions at beamline ID10B of ESRF using a Langmuir trough for air-water experiments and a specially designed new sample cell for the liquid-liquid interface experiments. Measurements at the air-water and preliminary experiments at the liquid-liquid interface were performed at the bromide x-ray absorption K-edge at the energy of 13.474 keV, as well as below it, at 13.274 keV. In Fig.1 reflectivity profiles of CTAB at the air-water interface at resonant energy and below are shown. A fit to the data using the program Parratt32 revealed a monolayer thickness of 1.62 nm for the cetyltrimethylammonium molecule with a thickness of the alkyl chain layer of 0.83 nm and the trimethylammonium headgroup layer of 0.79 nm. No clear evidence of the presence of bromide layer within the diffuse ionic layer could be detected.

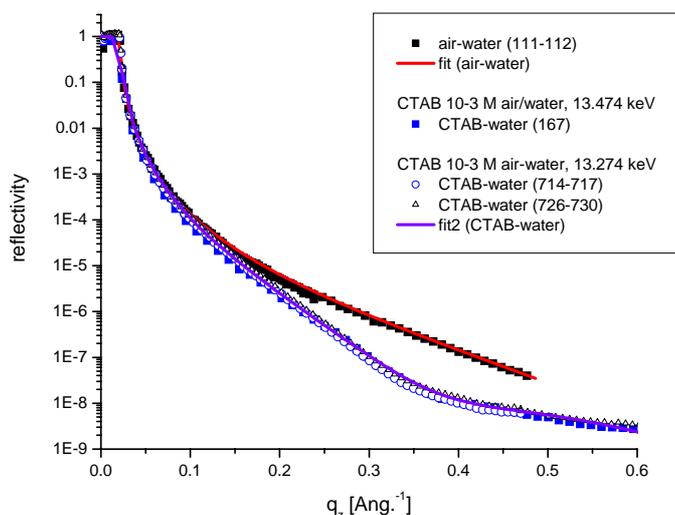


Fig.1. X-ray reflectivity curves of CTAB at the air-water interface at 13.474 keV (solid blue symbol) and at 13.274 keV (open blue symbols). For comparison reflectivity curve of the air-water interface at 13.474 keV is shown (solid black symbol). Straight lines are corresponding fits by Parratt32.