



	<b>Experiment title:</b> <b>Probing distribution of Br- ions in the CTAB monolayer using resonant X-ray reflectivity</b>	<b>Experiment number:</b> CH-2612
<b>Beamline:</b>	<b>Date of experiment:</b> from: 09-07-2008 to: 15-07-2008	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Oleg Konovalov	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Kamil Wojciechowski*, Warsaw University of Technology, Warsaw, Poland</b> <b>Thomas Gutberlet*, Juelich Centre for Neutron Sciences, Garching, Germany</b>		

## Report:

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 is 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 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. In these preliminary experiments, an aqueous solution of CTAB of  $10^{-3}$  M with or without addition of NaBr of  $10^{-1}$  M was used. The purpose of using such high concentrations was to gain information on a fully packed CTAB monolayer, which is necessary before the subsequent detailed studies planned in the nearest future. The two reflectivity curves at the resonant energy and below it practically superimpose each other. 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.

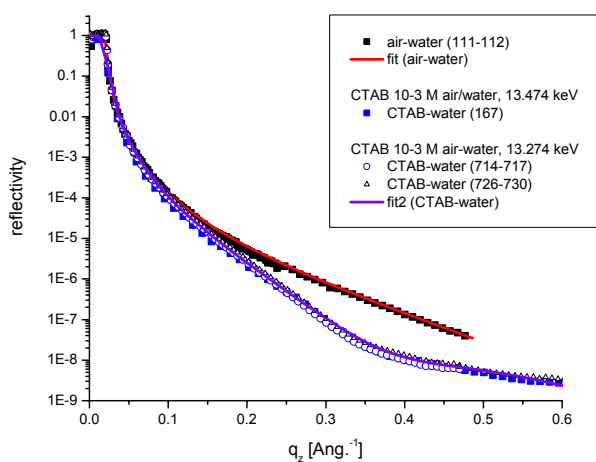


Fig.1: X-ray reflectivity curves of CTAB at the air-water interface at 13.474 keV (solid blue symbol) and at 13.274 keV (open blue symbols). For comparison reflectivity curve of the air-water interface at 13.474 keV is shown (solid black symbol). Straight lines are corresponding fits by Parratt32.

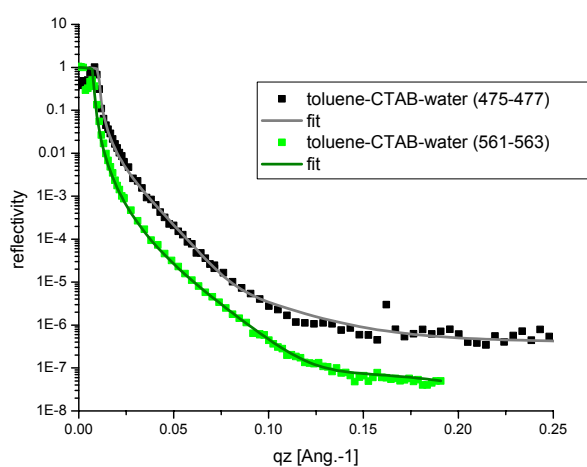


Fig. 2: X-ray reflectivity curves of CTAB at the toluene-water interface at 13.474 keV (solid black symbol) and at 13.272 keV (solid green symbol) and corresponding fits using Parratt32.

First measurements at a liquid-liquid interface of toluene-water were performed both at resonant energy and below it, using a circular sample cell developed at ID10B. In these preliminary test measurements, a fast decay of the reflectivity curves were shown (Fig. 2). Fits to the data using Parratt32 indicated the presence of a diffuse layer of 5.5 nm at the toluene-air interface at resonant energy. A CTAB monolayer could not be found. Below resonant energy a diffuse layer of 2.7 nm was found. Interpretation of this preliminary result is underway. Further experiments will be necessary to verify these first results and develop appropriate models of the ion distribution at the liquid-liquid interface.