ESRF	**Experiment title:** Alkyl-based imidazolium ionic liquids at the air-water interface: A X-ray reflectivity study	**Experiment number**: SC-4685
Beamline: ID10-EH1	**Date of experiment**: from: 12/12/2017 to: 12/18/2017	**Date of report**: 03/01/2018
Shifts: 18	**Local contact(s)**: Dr. Oleg Konovalov	*Received at ESRF:*

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Report for Proposal 75736:

As requested in the proposal, we succeed to measure specular X-ray reflectivity (XRR) and surface X-ray fluorescence (XRF) during several compression-decompression cycles of the two 1-alkyl-3methylimidazolium ionic liquids $[C_{18}mim]^+[N(Tf)_2]^-$ and $[C_{20}mim]^+[N(Tf)_2]^-$ on three different aqueous subphases (pure water, NaCl and $NaN(Tf)_2$ containing water). We applied the XRR and XRF techniques at 10 keV ($\lambda = 1.24$ Å, $\alpha_{critical} = 0.123°$, $Q_{critical} = 0.02175$ Å^{-1}) during 19 compression-decompression-cycles of $[C_{20}mim]^+[N(Tf)_2]^-$ on water to follow the evolution of the π-A-isotherm until the characteristic first plateau disappeared (**Figure 1**). Our previously gained grazing incident X-ray diffraction pattern and BAM images of $[C_{20}mim]^+[N(Tf)_2]^-$ indicated the formation of multilayers after the collapse plateau of the monolayer. As expected the obtained XRR data indeed strongly support this hypothesis. While there is almost no contrast compared to pure water at the maximum trough area (A_{max}, full expansion of the $[C_{20}mim]^+[N(Tf)_2]^-$ layer), there is a clear minimum in the reflectivity curve for the first compression plateau (**Figure 2A**). With ongoing compression-decompression cycles the plateau shifts to smaller areas and becomes short (**Figure 1**). At the same time the minimum in the reflectivity curves shifts to smaller Qz values indicating an increasing layer thickness. At minimum area (A_{min}, full compression of the $[C_{20}mim]^+[N(Tf)_2]^-$ layer) three well pronounced Kiessig fringes are visible (**Figure 2B**). This drastic change in the periodicity of the oscillation characterises a strong increase in the layer thickness, which might be caused by multilayer formation. The reflectivity curve measured on the expansion plateau looks similar the one obtained on the compression plateau, therefore it seem that the process is reversible. The longer oscillation period indicates a smaller layer thickness. The fully expanded $[C_{20}mim]^+[N(Tf)_2]^-$ layer has again barely a contrast compared to pure water.

Complementary to the XRR measurements, we recorded X-ray fluorescence spectra in dependence of the incidence angle in order to obtain information about the vertical distribution of $[N(Tf)_2]^-$. The bis(trifluoromethanesulfonyl)imide anion contains sulphur, which has its Kα line at 2.3 keV. The intensity of the sulphur peak, normalised by the elastic peak (10 keV), was plotted as a function of the incidence angle (**Figure 3A & 3B**). The obtained results confirm our expectations we gained from total reflection X-ray fluorescence (TRXF, $\alpha_{incidence} < \alpha_{critical}$) at the SIRIUS beamline at the Synchrotron SOLEIL. After nearly 50 compression-decompression-cycles the fluorescence intensity of sulphur decreases, which means that the $[N(Tf)_2]^-$ anions disappear from the near interfacial region (~ 40 Å). The setup at the ID10-EH1 beamline allowed us to vary the penetration depth of the X-ray beam in order to acquire different contributions from the bulk phase. The vertical distribution of the $[N(Tf)_2]^-$ anions at A_{max}, where the $[C_{20}mim]^+[N(Tf)_2]^-$ layer is fully expanded, shows a peak around $\alpha_{incidence} \sim 0.115°$ with an intensity of 0.16 arb. units. Within successive compressions and decompressions the sulphur intensity decreases drastically. Interestingly, the XRR curves taken at A_{min} (**Figure 2B**) indicates an increase in layer thickness, but in the fluorescence plot it seems like the amount $[N(Tf)_2]^-$ anions in the subphase are negligible (**Figure 3A & 3B**). In accordance with our GIXD pattern and BAM images, the most-likely scenario is multilayer formation leading to 3D crystal formation. As found and already published for $[C_{18}mim]^+[N(Tf)_2]^-$ [DOI: 10.1039/c6cc01368f].

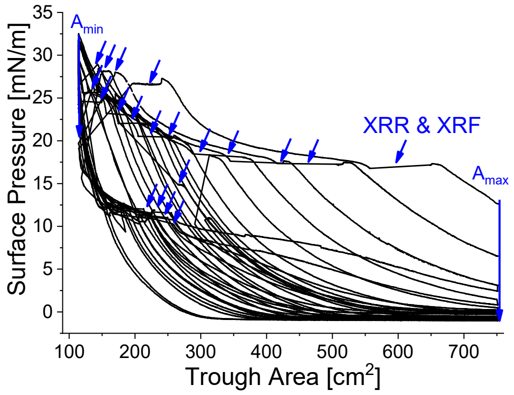

Figure 1: π-A-isotherm of $[C_{20}mim]^+[N(Tf)_2]^-$ layer on water. Blue arrows indicate the spots, were XRR and XRF scans were taken along the π-A-isotherm.

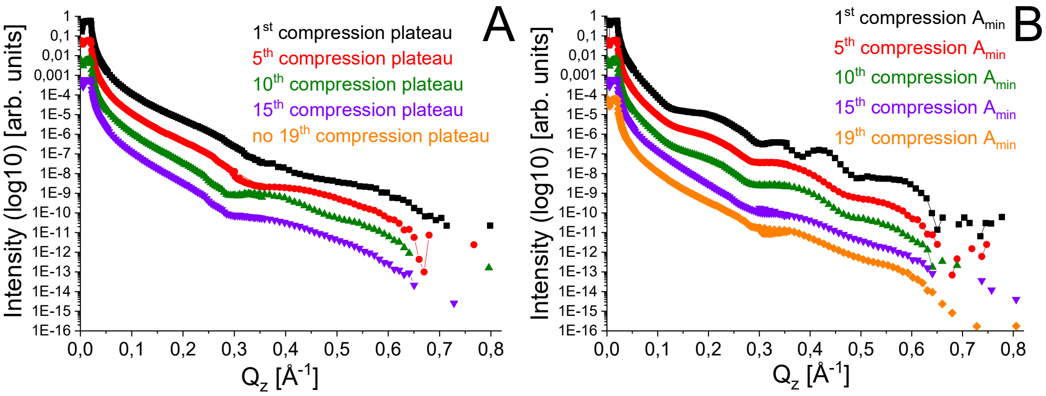

Figure 2: X-ray reflectivity curves of a $[C_{20}mim]^+[N(Tf)_2]^-$ layer on water. XRR scans taken **A)** on the 1st compression plateau and **B)** at minimum area. XRR curves are shifted vertically for clarity.

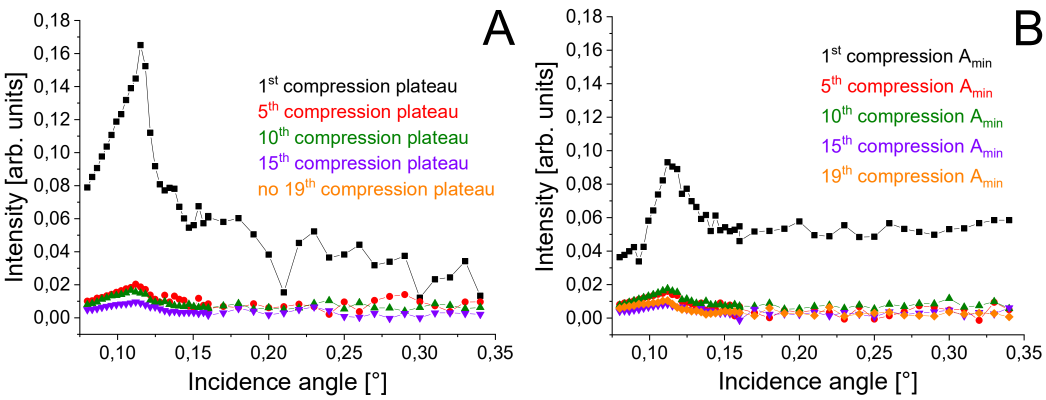

Figure 3: X-ray fluorescence spectra of a $[C_{20}mim]^+[N(Tf)_2]^-$ layer on water. XRF scans taken **A)** on the 1st compression plateau and **B)** at minimum area.

In conclusion, we obtained interesting results for two 1-alkyl-3methylimidazolium ionic liquids $[C_{18}mim]^+[N(Tf)_2]^-$ and $[C_{20}mim]^+[N(Tf)_2]^-$ on three different aqueous subphases (pure water, NaCl and $NaN(Tf)_2$ containing water), which are complementary to our diffraction experiments. Therefore, we are confident to publish these results soon. Further, we thank Dr. Oleg Konovalov very much for his excellent support and the ESRF for beamtime.