



	Experiment title: x-ray reflectivity and standing wave fluorescence spectroscopy with sulfate monolayers on ionic subphases	Experiment number: SI-1248
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Report:

Aim of the experiments

The counterion size has a pronounced effect on the potential of the electrical double layer (EDL) for highly charged monolayers at the air-water interface [1]. Experiments with mixtures of different electrolytes in the subphase suggest that small univalent counterions preferentially participate in the formation of the EDL and can even successfully compete with large divalent ions. Such behavior clearly contradicts the classical EDL model and obviously arises from packing density limitations for counterions in the vicinity of monolayers with high charge density.

The aim of the experiments was to determine relative amounts of different counterions in the EDL in a direct way. The initial idea was to combine anomalous X-ray reflectivity and standing wave fluorescence spectroscopy. However, finally we found that the usage of total reflection x-ray fluorescence (TRXF) is more productive for the particular study. Indeed, a TRXF experiment runs on a time scale of minutes, whereas the above mentioned combination requires many hours.

Experimental

The beam (exciting photon energy of 22.5 keV) was highly collimated in vertical direction (thickness 0.018 mm, divergence less than 0.003 degrees) and was sent to the monolayer surface at a fixed angle of 0.022 degrees (approximately 1/3 of the critical angle for total reflection). A Langmuir trough was equipped with a moveable single barrier. The surface pressure of the monolayer was measured using a Wilhelmy plate and was kept constant during the experiment. The beam reflected from the liquid surface was detected by a scintillation (NaI) detector for vertical adjustment of the system. The fluorescent signal was measured by a Peltie cooled ROENTEC drift diode Si detector placed above the water surface at a distance of ca. 12 mm.

Results

The TRXF spectra in figure 1 elucidate the role of the counterion size in the competition between different ions in the EDL formation at a highly negatively charged monolayer of behenylsulfate (BS). The use of the spectrum of a single counterion in the subphase as a calibration reference gives the possibility to estimate the relative amounts of counterions in the EDL when two (or more) counterions are present in the subphase. The relative amount of Ba^{2+} (Fig. 1, top) is approximately 0.9 in the EDL using equal concentrations of Ba^{2+} (relative amount of 0.5) and Ca^{2+} for the preparation of the subphase. Thus, the smaller Ba^{2+} is significantly enriched in the EDL compared to Ca^{2+} . The relative amount of the small univalent Cs^+ (Fig. 1, bottom) is approx. 0.4 in the presence of Ca^{2+} and 0.15 in the presence of Ba^{2+} . It is worth noting that the classical model gives only 0.06 for both cases. More precise estimation requires taking into account variations in the monolayer packing density and intensity of exciting X-ray field in the EDL region (both are rather small).

The composition of the EDL at highly positively charged monolayers of protonated eicosylamin (ECA) using simple inorganic anions as counterions has also been investigated. In all experiments, the pH of the subphase was adjusted to approx. 4 to ensure full protonation of the ECA monolayer.

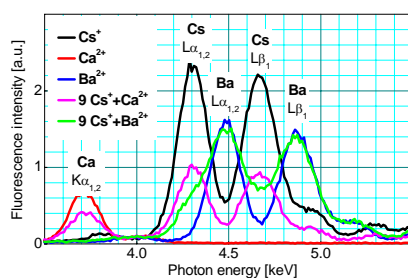
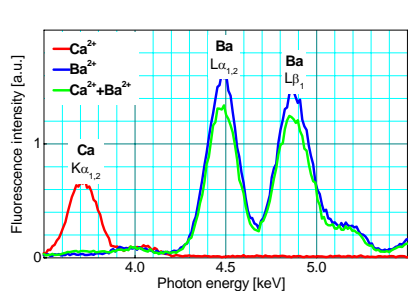


Figure 1

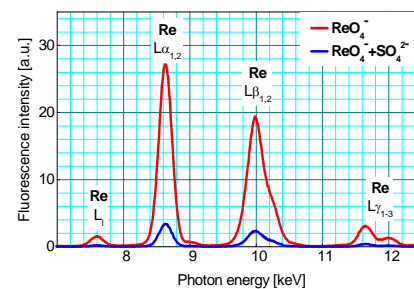
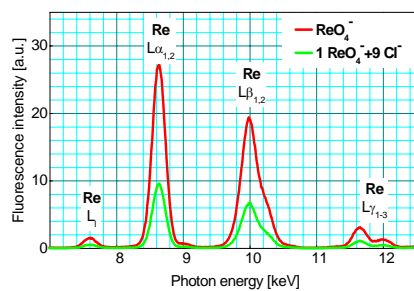


Figure 2

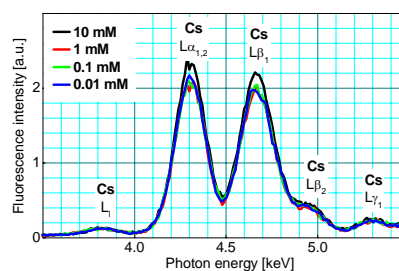


Figure 3

Representative TRXF spectra are presented in figure 2 (contribution of the bulk subphase is negligible as in the case of the BS monolayer). Since Cl^- and SO_4^{2-} have only weak fluorescence lines below 3 keV they appear “invisible” and only the strong fluorescence of ReO_4^- is observable. However, the amounts of “invisible” counterions can be easily estimated from the decrease of ReO_4^- fluorescence, since the total charge of counterions in the EDL (per unit area) is equal to the monolayer surface charge density, i.e. remains approximately constant for the different compositions of the subphase. Figure 2 (top) shows the competition of two univalent counterions. The fraction of ReO_4^- in the EDL is approx. 0.4, whereas it is only 0.1 in the subphase. Hence, the small ReO_4^- preferentially participates in the EDL formation compared to Cl^- which is much larger (due to strong hydration). Figure 2 (bottom) shows that the fraction of ReO_4^- in the EDL is approx. 0.1 whereas the classical Gouy-Chapman theory predicts only 0.008 for this case. Thus, the small univalent ReO_4^- anion can successfully compete with the larger divalent SO_4^{2-} anion.

Figure 3 supports the classical model, which predicts that most of the counterions in the EDL at highly charged surfaces are located close to the surface. TRXF spectra (penetration depth of approx. 50 Å) for highly negatively charged BS monolayers on subphases with different concentrations of CsCl confirm that the amount of Cs^+ counterions is independent of the electrolyte concentration. Obviously, the integral amount of counterions in the peripheral part of EDL profiles is negligible compared with the inner part of the EDL. More detailed data treatment is in progress.