Hofmeister effect in adsorption of CTAB at fluid-fluid interfaces (ESRF exp. CH-3069)

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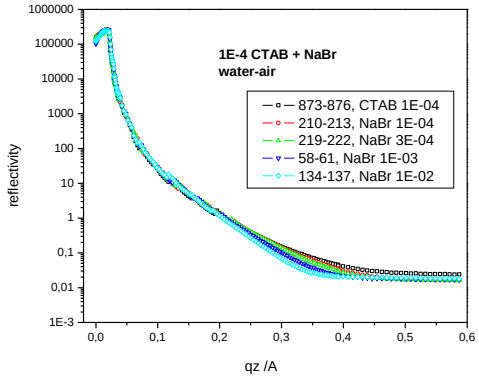
Studying adsorption of cationic surfactants at water-air interface is a convenient method for investigation of mechanism of generation of electrical potential difference at various interfaces, e.g. at water-membrane interface in Ion Selective Electrodes (ISE). In the latter, tetraalkylammonium salts are major components of anion-selective membranes, and the analytical signal of ISEs is generated through the charge separation at the interface between the ion selective membrane and the test solution. The selectivity of such ISEs follows the same order as the Hofmeister series, a well known in biochemistry and colloid chemistry ordering of ions according to their effect on different phenomena, like protein solubility, colloid stability, etc.

In the present study we have extended our previous preliminary results on analysis of anion-specific effects (Hofmeister effect) at water-air and water-oil interfaces. The experimental protocol consisted of measuring both X-ray reflectivity and X-ray fluorescence from the water-air interface. Some measurements with X-ray reflectivity were also performed at water-tetradecane interface.

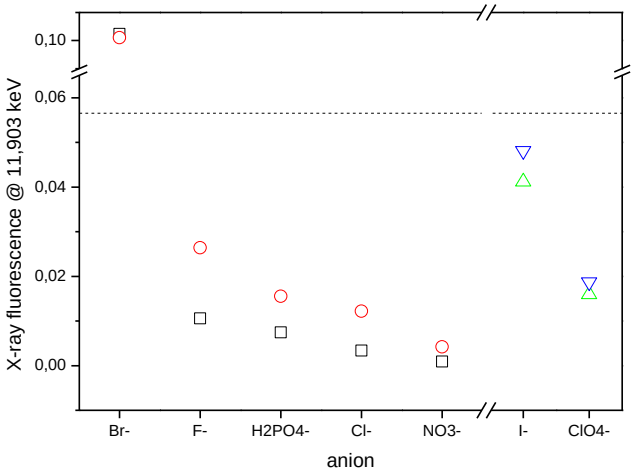
The model tetraalkylammonium salt, cetyltrimethylammonium bromide (CTAB) was chosen and studied with help of Langmuir trough installed in the ID10 B beamline. The effect of anions was studied at fixed concentration of CTAB, by adding respective sodium salts (NaX, with X^-=Br^-, Cl^-, F^-, $H_2PO_4^-$, NO_3^-, I^-, $ClO4^-$) to the aqueous phase. The anions were chosen to cover the broadest range of the Hofmeister series. In accordance with expectations, X-ray reflectivity revealed the presence of a thin (19 A) monolayer of CTAB at the water-air interface. With increasing bulk concentration of CTAB, the scattering length density of the monolayer was decreasing, suggesting formation of more and more densely packed layer. The same was observed at water-tetradecane interface, where experiments were performed in a special dedicated liquid-liquid cell.



Upon addition of sodium salts of different anions, the reflectivity curves were slightly changing depending on the type of concentration of anion added, clearly pointing to some anion-specificity of the process of adsorption of CTAB/NaX mixture, and to at least partial penetration of X- anions added with the salts, into the monolayer. Due to rather low electronic contrast between water and CTAX monolayers, the quantitative analysis of the Hofmeister effect based solely on X-ray reflectivity is,

however, not possible.

More quantitative information was obtained from X-ray reflectivity measurements in the total reflection geometry (Total Reflection X-ray Fluorescence, TRXF). Thanks to a X-ray penetration depth being comparable to the thickness of electrical double layer formed at the water-air interface, this technique allowed us to quantify surface concentration of bromide ions as counterions in the Gibbs monolayers of CTAX. Fig. below presents the selected Br fluorescence intensity for a series of solutions with fixed CTAB concentration (10^{-4} M) and different concentrations of added salts. While addition of NaBr results in an increase of Br emission line intensity, other anions decrease it to different extent, showing quantitaively their different ability to replace Br- ions from the adsorbed Stern layer (i.e. the molecular basis of the Hofmeister effect).



The experimental results are in very good agreement with the surface and interfacial tension, analysed in the framework of the Stern model of electrical double layer with specific co-adsorption of anions in the Stern layer. To our knowledge the present study provides a first unqeuivocal proof of this specific adsorption, which has been postulated in the literature on the basis of different indirect experimental results.