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Halide anion dependence of ionic surfactant adsorption in air/water interface

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— It was recently proposed that there is surface excess of halide anions at the air/water interface, and more surface excess of I^- than Br^- or Cl^-, which cannot be explained by Debye-Huckel theory. In case of charged surfaces such as Gibbs monolayer consisting of cationic surfactant molecules, surface excess of anions can also be expected. In this study, by using surface-sensitive grazing angle X-ray fluorescence in conjunction with surface tension measurement, we investigated adsorption behavior of [C_{12}mim]Cl, [C_{12}mim]Br, [C_{12}mim]I aqueous solutions, in which the surface is first covered by [C_{12}mim]$^+$ cations at low concentrations, and the adsorption of the halide anions to this charged interface would follow with the increase in the concentration of solutes. From the surface tension measurements, it was observed that critical micelle concentration of [C_{12}mim]I solution was 4.6 mM, much smaller than that of [C_{12}mim]Cl (16.7 mM) indicating surface activity of surfactant increases with size of halide anions. From X-ray fluorescence, surface excess of halide anion was measured quantitatively from the interface of these solutions. By putting NaCl and NaI in [C_{12}mim]I and [C_{12}mim]Cl solutions, respectively, competition between Cl^- and I^- adsorption was investigated, to find that I^- has stronger adsorption on the charged surface than Cl^-.

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