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Superchaotropicity : grafted surface to probe the adsorption of nano-ions

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Nano-ions (NIs) are ionic species or clusters of nanometric size. Their low charge density and the delocalization of their charges give special properties to some of NIs belonging to chemical classes of polyoxometalates (POMs) or boron clusters (BOCs). They have the particularity of interacting non-covalently with neutral hydrated surface or interfaces such as assemblies of surface-active molecules (micelles, vesicles, lyotropic liquid crystals), foam bubbles or emulsion droplets. This makes possible to classify those NIs in the Hofmeister series as superchaotropic ions. The mechanism of adsorption is complex, linked to the simultaneous dehydration of the ion and the molecule or supramolecular assembly with which it can interact, all with an enthalpic gain on the free energy of the system. This interaction process is reversible and is sufficiently pronounced to induce changes in molecular and supramolecular shape or conformation, phase transitions in the liquid phase, all at sub-millimolar ionic concentrations. This new property of some NIs opens up new possibilities for applications in fields as varied as biochemistry for solubilization, recovery of metals of interest by foams in the form of NIs... In order to better understand the physico-chemical mechanisms at the origin of this interaction, we use silicon wafers functionalized by non-ionic oligomers (polyethylene glycol chains or PEG) to study in situ by X-ray reflectivity this interaction of NIs with the grafted chains. A first study carried out at ESRF (European Synchrotron Radiation Facility) on BM32 and has shown that the adsorption of the NIs, such as POMs, characterized by a very strong interaction at low concentrations. We aslo noticed this tendancy with BOCs on X-ray reflectivity lab set. Moreover the distribution of the NIs within the grafted PEG chain layer was quantify. These results are very encouraging and confirm what has been observed on soft interfaces such as micelles or foams. The next step will be to explore a larger family of NIs. The possibility to play on the density, length and chemical nature of the grafted chains makes this system an ideal tool to provide kinetic and thermodynamic information to decipher the complex mechanisms at the origin of this adsorption.

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Thin films and interfaces in soft matter and materials science

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