Macro- and nano-scale electrostatics govern self-assembly, interactions, and self-healing at charged aqueous surfaces

Pascal Tomasella [a], Giovanni Lucifora [a], Roberta Ruffino [a], Carlo Carbone [b], Libero Liggieri [b], Eva Santini [b] and Giovanni Li Destri [a]

[a] University of Catania, Department of Chemical Sciences
[b] Italian National Research Council (CNR), Institute of Condensed Matter Chemistry and Technologies for Energy, Unit of Genova

giolides@unict.it

Understanding how the electrostatic interactions influence the structure and properties of aqueous surfaces is of fundamental importance in many fields spanning emulsion/foam stabilisation, catalysis, materials science, and biochemistry. Yet, the role played by the ionic strength and charged species is poorly understood.[1] Here, we apply a macro and nanoscale structural and electrostatic characterisation to elucidate how the ionic strength and the cation charge modulate the organisation and electrostatic response of negatively charged silica nanoparticles at the water surface.[2] We identify a self-regulation mechanism whereby the steady-state inter-particle distance is dictated by a characteristic mesoscopic electrostatic potential and a fixed single-particle repulsive energy, irrespective of ion identity and ionic strength. Changes in the electrolyte composition set the nanoparticle surface excess, which adjusts to compensate for changes in the interfacial dipolar strength. Furthermore, the behaviour of the monolayer under mechanical deformation demonstrated the onset of composition-dependent short-range inter-particle attractions as the ionic strength or the cation charge increased. Such attractions also determine the monolayer relaxation mechanism upon compression. In the presence of strong attractions, the monolayer relaxes via the formation of two-dimensional clusters; vice versa, when nanoparticles repel each other, the relaxation leads to the formation of isolated nanoparticles at the surface. We will demonstrate that the two relaxation mechanisms markedly influence the monolayer's self-healing capabilities upon mechanical compression. This provides further tools to build aqueous surfaces with tailored structure, properties and dynamical response to stimuli.

Keywords:
Interfacial electrostatics, Ion effect, Electric double layer, Dipolar interactions, Interfacial screening

References:

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