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Polyelectrolyte brushes in hypersaline environments: Probing underscreening with neutron reflectometry

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Electrostatics plays a fundamental role in a wide range of natural phenomena and is crucial for understanding the interactions between charges in many biological, chemical, and physical systems. Despite being poorly understood, hyper-saline environments are ubiquitous in nature and myriad technological processes. In particular, polymer morphology is critically important in these hyper-saline regimes, with the atomic level interactions between the polymer, solvent and salt determining the overall polymer nanostructure, ultimately governing applications such as lubrication and protein activity.

Recent experiments have revealed that the theory encompassing classical electrostatics (e.g., DLVO theory) breaks down at high salt concentrations.[1, 2] For monovalent ions at high concentration regimes, a minimum exists in the electrostatic decay length, beyond which underscreening has been observed, where the range of electrostatic interactions is greater than the anticipated Debye length.[1, 3, 4] This underscreening phenomenon is enhanced with valency and concentration.

To probe underscreening, we employed a strong cationic and a strong anionic polyelectrolyte brush as exemplars.[5] In the context of polyelectrolyte brushes, underscreening, or re-entrant behaviour, presents itself as a non-monotonic change in brush thickness with increasing salt concentration; an initial decrease in brush thickness at intermediate concentrations followed by a subsequent increase at high concentrations. The influence of both mono- and multivalent ions on the electrostatic decay length at high salt concentrations was examined by probing polyelectrolyte brush conformation in response to electrolyte. Neutron reflectometry (NR) and spectroscopic ellipsometry (SE) revealed that in hypersaline environments, both cationic and anionic polyelectrolyte brushes exhibit re-entrant behaviour. Both NR and SE showed a non-monotonic change in brush thickness as a function of electrolyte concentration. Interestingly, however, for the first time NR revealed that the structure of the *swollen* polyelectrolyte brush is different in electrolytes of low and high concentration.

References

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Thin films and interfaces in soft matter and materials science

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