Aggregation of Heteropolyanions in Aqueous Solutions Exhibiting Short-Range Attractions and Long-Range Repulsions

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Short-range attractions and long-range repulsions (SALR) between charged particles play critical roles in processes of biological and industrial interest, and are crucial to understand the structure of soft materials containing proteins, DNA, colloids, and polymers.

By combining small-angle X-ray scattering and atomistic molecular dynamics simulations, we studied the structural architectures of simple charged systems in the form of spherical, Keggin-type heteropolyanions (HPAs). The coexistence of non-associated monomers and randomly percolated monomers are conclusively justified both experimentally and by atomistic simulations. Moreover, the SALR is shown to drive the stability of aggregates composed of Si-HPAs, which are -3*e* charged. Atomistic simulations revealed the atomistic scale origins of SALR between Si-HPAs. The short-range attractions result from water or proton-mediated hydrogen bonds between neighboring Si-HPAs, whereas the long-range repulsions are due to the distributions of ions surrounding the Si-HPAs.

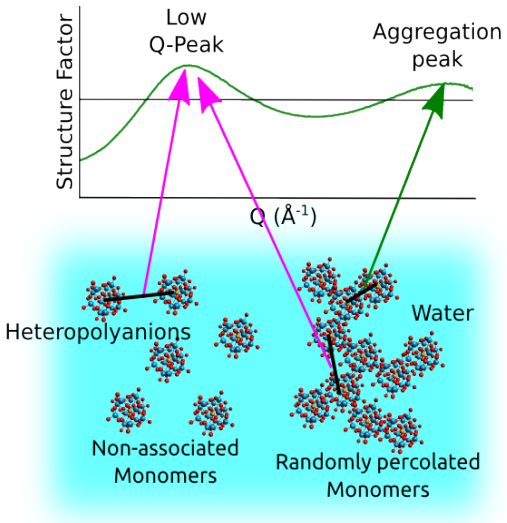

Figure: Typical SAXS/SANS structure factor showing two distinct peaks corresponding to different correlations in the solution of particles interacting via short-range attractions and long-range repulsions. The coexistence of non-associated monomers and randomly percolated monomers are conclusively justified in the present work.

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