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Ion Pairing Controls Ion Fate at Interfaces and Under Confinement

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Ion pairing is a fundamental molecular process governing ion distribution, adsorption, and reactivity at mineral–water interfaces and under nanoconfinement, yet its thermodynamic role across these environments remains poorly resolved. Here, we present a unified molecular-scale investigation of ion pairing at charged interfaces and within neutral nanopores using atomistic molecular dynamics and enhanced sampling simulations. At positively charged layered double hydroxide interfaces, ion pairing between adsorbed counterions and like-charged co-ions enables co-ion penetration into the Stern layer. This penetration is strongly concentration dependent: dilute systems remain surface-dominated and exclude co-ions, whereas increased electrolyte concentration compresses electrostatic screening, stabilizes contact ion pairs, and allows monovalent co-ions to access interfacial regions according to their hydration energetics ($K^+ > Na^+ > Li^+$), while strongly hydrated divalent ions remain excluded.

Complementary simulations in neutral nanopores reveal a distinct but related mechanism: ion pairing governs whether ions partition into confinement at all. In hydrophilic gibbsite nanopores, individual ions are not thermodynamically favored, yet paired ions behave as oriented dipoles that align with confined water structure, making ion-pair incorporation energetically preferred relative to bulk solution. In contrast, partially hydrophobic kaolinite nanopores suppress both ion and ion-pair partitioning because disruption of the hydrogen-bond network is unfavorable.

Together, these studies demonstrate that ion pairing is not merely a bulk-solution phenomenon but a context-dependent mediator that couples electrostatics, hydration, and surface chemistry to regulate ion accessibility, adsorption, and transport across interfaces and confined spaces. The results establish a mechanistic framework describing a continuum from surface-controlled exclusion to screening-enabled association and confinement-stabilized dipolar alignment. This framework provides predictive insight for interfacial processes central to energy storage, membrane separations, geochemical reactivity, and critical-mineral recovery, where ion correlations—not just single-ion properties—govern macroscopic behavior.

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