

**A combined flow microcalorimetry
and surface complexation modeling
study of ion exchange
thermodynamics at the rutile-water
interface.**

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Flow microcalorimetry was used to investigate the energetics associated with Rb⁺, K⁺, Na⁺, Cl⁻ and NO₃⁻ exchange at the rutile-water interface. Heats of exchange reflected differences in bulk hydration/dehydration enthalpies (Na⁺>K⁺>Rb⁺, and Cl⁻>NO₃⁻) such that exchanging Na⁺ or Cl⁻ from the surface was exothermic, reflecting their greater bulk hydration enthalpies. Exchange heats were measured at pH 2, 3.25, 5.8, and 11 and exhibited considerable asymmetry as well as pH dependence. These trends were rationalized with the aid of a molecularly-constrained surface complexation model (SCM) which incorporated the inner-sphere binding observed for the cations on the rutile (110) surface. Explicitly accounting for the inner-sphere binding configuration differences between Rb⁺, K⁺, and Na⁺, as well as accompanying differences in negative surface charge development, resulted in much better agreement with measured exchange ratios than by considering bulk hydration enthalpies alone. The observation that calculated exchange ratios agreed with those measured experimentally lends additional credence to the SCM. Consequently, flow microcalorimetry and surface complexation modeling are a useful complement of techniques for probing the energetics associated with ion exchange and adsorption processes, and should also serve to help validate molecular simulations of interfacial energetics.