Dynamics of organo-mineral interactions on the metal oxide-solution interface as studied via binding energetics

TODD L. LONGBOTTOM[1], OMAR R. HARVEY[1]

[1]Department of Geological Sciences, Texas Christian University, Fort Worth, TX, USA

This study seeks to elucidate the dynamics of binding energetics of a suite of organic molecules (Na salts of carboxylic acids) on amorphous SiO_2 using Flow Adsorption Microcalorimetry (FAMC). Specifically, we have combined energetics-based reaction parameters with Eyring-Polyanyi and vant Hoff equations to assess bonding characteristics of these systems (i.e. bonding trajectory, extent, mechanism, and bonding strength). Our FAMC analyses and exotherm/endotherm deconvolution suggests 4 - 5 unique bonding processes for all solutes across pH 3 - 7. Reaction duration appears to be controlled primarily by the pH of solution, where increasing pH drives a shorter reaction time – possibly owing to the occupation of available binding sites at low pH. Reactions generally vary by trajectory according to organic structure of solutes, where Na-butyrate binding was revealed to be an endothermic process, while Na-acetate, Na-benzoate, and Na-oxalate binding were exothermic. For this reason, binding trajectories are likely dependent upon organic functional group(s), where nonpolar alkyl chains promote enthothermic binding, while methyl, aromatic, and carboxylic groups appear to promote an exothermic trajectory. Overall heats of binding were low – ranging +180 to -427 J mol^{-1}, approximately an order of magnitude lower than ion exhange, and 2 orders of magnitude lower than ligand exchange. These results can support the development of computational models of organo-mineral interactions as well as facilitate the further development of experiment-driven understanding of bonding dynamics.