

Proportionalities Among Aqueous Metal-Organic Complex-Forming Reactions

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Aqueous solutions in diverse natural systems can contain hundreds of organic ligands and dozens of metal cations that combine to form thousands of molecular complexes. A challenge is to include all such species in aqueous speciation, mass transfer, reactive transport, and metabolic energy models. Doing so requires methods to estimate equilibrium constants for thousands of metal-ligand reactions that have not been studied experimentally. Luckily there are systematic behaviors among thermodynamic properties that enable such estimates.

We start by assuming that interactions among anionic ligands and metal cations are proportional to the interactions of those ligands with H^+ . The basis for this assumption is that there will be variable strengths of interactions among ions in solution, and an individual ligand is identical in all cases of complex formation with metal cations. From the perspective of a cation, it will interact differently with various anionic ligands in solution. We propose that correlations among association constants for metal-ligand complex formation for pairs of ligands will be proportional to the ratio of equilibrium constants for their acid association reactions. This observation allows development of novel estimation methods for dozens of anionic organic ligands including carboxylates and amino acid anions. We observe that proportionalities vary with increasing differences in ligand structure in ways that are complementary to shifts in equilibrium constants for their acid association reactions. As a result, it is possible to predict proportionalities from molecular structures for ligands that have not been extensively studied via experiments. Furthermore, it becomes possible to identify cations that interact uniquely with certain ligands, perhaps due to nuances in their electronic structures. These details aside, new correlation algorithms derived from the wealth of experimentally determined association constants allow estimates for hundreds of metal-ligand complexes for which experimental data are limited. As a result, models of hydrothermal solutions can be far more inclusive of the variety of solutes than previously possible. In addition, these advances enable speciation, mass transfer, reactive transport, and metabolic energy calculations within cells of extremophiles thriving in hydrothermal systems.