Metal Complexes: Their Free Energies and Their Reactivities in Solution

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Frontiers in Geochemistry
Seminar Series

Presented by…

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A metal ion dissolved in solution experiences correlations with solvent molecules and other dissolved ions, the strengths and numbers of which determine its solubility and stability. Aided by a number of analytical techniques, notably UV/visible and XAFS spectroscopies, a picture has emerged over the last several decades in which a dissolved metal ion is understood to have a near-neighbor ligation sphere that is relatively strongly bound and is the primary contributor to the reactivity and energetics of the ion. Indeed much of the theoretical modeling done to provide a framework for predicting metal-ion behavior in solution includes a detailed description of this first coordination sphere. Although it has been recognized that there can been second and more distant ligation spheres, they have been largely ignored, in part because of the lack of metrical information about their structure, and in part because it is thought that their contribution is minimal to the overall energetics of the dissolved metal ion.

We have recently begun to employ high-energy x-ray scattering (HEXS) as a probe of metal correlations in solution. Unlike the techniques used to date, HEXS is sensitive to correlations in solutions that extend out to 1 nm or longer. Using this technique we are able to extract metrical information for inner-sphere environments within an error of about 2%, and second- and higher-sphere information to about 5%. Changes in coordination as a function of solution conditions can now be probed with a precision sufficient to provide the quantitative information needed to determine thermodynamic stability constants for simple metal-ion reactions. For example, HEXS provides quantitative structural information that has been used to determine independent stability constants for the inner and outer sphere complexes simultaneously present in solution. Selected recent results will be presented that provide new perspectives on dissolved ions and their complexes. This work is supported by the DOE, OBES, Chemical Sciences, under contract DE-AC02-06CH11357.

More info:

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