

## Speciation of metal ions in water: comparison of their reactivities with oxygen-donor hard ligands

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Complexation of metal cations with ligands such as hydroxide ion, carbonate ion, carboxylate ion, and phosphate ion is one of the most important factors controlling behaviors of metal ions in natural environment. Previous studies showed that these ligands were classified as "intermediate hard ligands" having oxygen donor, which favors to form ionic bonding. However, it was found that the reactivity of these ligands depends on ionic radius and that there is a difference of the reactivity between hydroxide ion and other intermediate hard ligands such as carbonate and carboxylate. For example, among divalent alkaline earth metal ions, Mg<sup>2+</sup> mainly precipitates as hydroxide (brucite), while Ca<sup>2+</sup> prefers to form carbonate (calcite) or phosphate (apatite) minerals rather than hydroxide. However, quantitative discussion on the selectivity of metal cations has not been performed.

In this study, we evaluated the standard Gibbs free energy, entropy, and enthalpy for the complex formation of hydrated metal cations with these ligands based on a critical thermodynamic database. As a result, we found that the entropic contribution to the free energy was large in the case of hydroxide complex of smaller cation. In contrast, the entropic contribution to the free energy was small in the case of hydroxide complex of larger cation and other complexes. In addition, the enthalpy contribution was not significant in this reaction. In the aqueous complexation reaction, entropy was controlled by the number of water molecules replaced by the ligand, suggesting that hydroxide complex for large cation was not stable due to the small effect of dehydration.

This suggestion was confirmed by quantum mechanical calculations, which was performed with B3LYP/6-311+G\* level using Gaussian 09. We calculated distance between metal (M) in the center and oxygen (O) in the ligand with the increase of number of water molecules placed in the vicinity of the metal ion. As a result, it was found that the M-O distance for hydroxide complex is larger than that of carbonate in the case of larger cation and vice versa. This means that hydroxide prefers to form outer-sphere complex for larger metal ion, which is not the case of other intermediate hard ligands. This result is consistent with what we suggested based on the thermodynamic data.

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