

水圏での金属イオンのスペシエーション：HSAB理論における中程度にハードな配位子の更なる分類

Speciation of metal ions in hydrosphere: Further classification of intermediately hard ligands in HSAB theory

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Complexation of metal cations with oxygen donor ligands such as hydroxide ion, carbonate ion, phosphate ion, and carboxylate ion is one of the most important factors controlling their behaviors in hydrosphere. Turner (1981) classified these ligands as “intermediately hard ligands” in HSAB (hard and soft acids and bases) theory. However, we found that the reactivity of hydroxide ion greatly depends on cation's ionic radius, which results in distinguishing this ligand from the other intermediately hard ligands. Taking divalent alkaline earth metal ions as an example, Mg^{2+} mainly precipitates as hydroxide (brucite), whereas Ca^{2+} prefers carbonate (calcite) or phosphate (apatite) to hydroxide, but quantitative discussion on the mechanism has not been performed.

In this study, we evaluated the standard Gibbs free energy change of reaction ($\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0$) on the complexation of hydrated metal cations with above ligands, based on thermodynamic data. The results revealed that the entropic contribution to the stabilization was large for hydroxide complexes of smaller cations. Since the entropy in aqueous complexation reaction is controlled by the number of water molecules released to the solution possibly due to replacement of the water molecules by inner-sphere complexation, it is suggested that hydroxide complexes of larger cations are less stable due to the small effect of the dehydration.

In order to support this suggestion, we conducted quantum chemical calculation, using Gaussian 09. The distance between hydrated metal cation (M) and oxygen of ligand (O) was calculated for several ions. The results showed that the average M-O distance of hydroxide complex increased with the increase of cation's ionic radius more remarkably than that of the other complexes such as carbonate ion. This means that hydroxide favors to form outer-sphere complex for larger cations, which is consistent with our suggestion based on the thermodynamic data.

キーワード：スペシエーション、HSAB理論、量子化学計算、内圏錯体、外圏錯体

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