Ab initio Molecular Orbital Calculations of Reduced Partition Function Ratios of Hydrated Lithium Ions in Ion Exchange Systems

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Molecular orbital (MO) calculations at the HF/6-31G(d) level were carried out for the aquolithium ions, $Li^{+}(H_2O)_n$ (n = 3, 4, 5, 6, 8, 10 and 12) and the aquolithium ions interacting with the methyl sulfonate ion (MeS⁻), $Li^{+}MeS^{-}(H_2O)_n$ (n = 0, 3, 4, 5, 6, 7, 8 and 10) which were, respectively, intended to be substitutes for lithium species in the solution and resin phases of ion exchange systems for lithium isotope separation. For each of the species considered, at least one optimized structure with no negative frequency was obtained, and the ⁷Li-to-⁶Li isotopic reduced partition function ratio (RPFR) was estimated for the optimized structure. The solvation number in the primary solvation sphere in the resin phase. Additional water molecules moved off to the secondary solvation sphere. It was found that consideration on the primary solvation sphere alone was insufficient for estimations of reduced partition function ratios of aquolithium ions. Although the agreement between the experimentally obtained lithium isotope fractionation and the calculated results is not satisfactory, it is pointed out that the HF/6-31G(d) level of the theory is usable for elucidation of lithium isotope effects in aqueous ion exchange systems.

Key words: Ab initio Molecular Orbital Calculations; Reduced Partition Function Ratios: Hydrated