

Ab initio QM/MM molecular dynamics simulation of preferential K⁺ solvation in aqueous ammonia solution

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A combined *ab initio* quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulation has been performed to investigate the solvation structure of K⁺ in 18.4% aqueous ammonia solution. The chemically most relevant region, the first solvation sphere of K⁺, was treated by Born–Oppenheimer *ab initio* quantum mechanics using LANL2DZ basis sets, while the rest of the system was described by classical pair potentials. Within the first solvation shell of K⁺, the QM/MM simulation reveals a polyhedral structure with an average coordination number of 7.6, consisting of 6.7 water and 0.9 ammonia molecules, compared to the corresponding value of 8.7 composed of 5.3 water and 3.4 ammonia molecules obtained by classical pair potential simulation. The QM/MM results, in contrast to the classical simulation, clearly indicate a preference for water ligands and a higher flexibility of ligand arrangements in the first solvation shell of the ion. The preference for ligands is discussed on the basis of detailed simulation results. In addition, a “structure-breaking” behavior of the ion is well recognized by the detailed analysis on ligand exchange processes and the mean residence times of the ligands surrounding the ion.