Preferential solvation of Ca^{2+} in aqueous ammonia solution: Classical and combined *ab initio* quantum mechanical/ molecular mechanical molecular dynamics simulations

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Classical and combined quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulations have been performed to investigate the solvation structure of Ca^{2+} in 18.4% aqueous ammonia solution. The classical molecular dynamics simulation has been carried out based on pairwise additive potentials. For the QM/MM scheme, the first solvation sphere of Ca^{2+} is treated by Born–Oppenheimer *ab initio* quantum mechanics using LANL2DZ basis sets, while the rest of the system is described based on classical pairwise additivity. The results indicate the importance of the QM treatment in obtaining a reliable geometrical arrangement as well as the correct coordination number of the solvated ion. Within the first solvation sphere of Ca^{2+}, the QM/MM simulation reveals a polyhedral structure with an average coordination number of 7.2, consisting of 5.2 water and 2 ammonia molecules, compared to the corresponding value of 9.7 composed of 6.7 water and 3 ammonia molecules obtained by classical pair potential simulation. The preference for ligands is discussed on the basis of detailed simulation results.