

Preferential Solvation of Li^+ in 18.45 % Aqueous Ammonia: A Born–Oppenheimer *ab Initio* Quantum Mechanics/Molecular Mechanics MD Simulation

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A molecular dynamics simulation using a mixed *ab initio* quantum mechanics/molecular mechanics formalism has been performed in order to obtain refined structural properties for a $\text{Li}(\text{I})$ ion in 18.45% aqueous ammonia solution. Using a double- ζ valence basis set for the quantum mechanically described first solvation shell including the ion, a tetrahedral structure with three water and one ammonia ligand is observed, in contrast to the octahedral structure with three water and three ammonia ligands predicted by classical pair potential simulation. This can be considered as further proof for the importance of nonadditive n -body effects for a proper description of ions in solution, even if they are only single charged. Further structural data and the preference for water ligands are discussed on the basis of detailed simulation results.

Introduction

As a result of the continuous increase of computer capacity and performance, more sophisticated and accurate simulation techniques incorporating quantum mechanical algorithms have become accessible for the study of condensed systems.^{1–7} A coupled semiempirical molecular orbital and molecular mechanics model has been applied for a wide range of neutral organic molecules in aqueous solution,² and the performance and suitability of combined quantum mechanical and molecular mechanical models concerning solvent effects in chemical reactions in solution have been discussed extensively.³ Among these, the Born–Oppenheimer *ab initio* quantum mechanics/molecular mechanics approach has proven especially suitable for the study of structural and dynamic properties of solvated ions by molecular dynamics simulations.^{4–7} This technique includes the crucial many-body contributions for the whole first solvation shell of the ions and has led to some major revision of previous results obtained for solvated ions by pair potential and even three-body corrected simulations. The many-body terms can effect drastic changes in the composition of the solvates, in particular concerning the coordination numbers, and have a strong influence on the orientation of the ligands as well.^{4–7} Further, they are needed to reproduce well-known chemical properties of solvated ions as structure-making and structure-breaking effects.⁷

Since such properties and structural details have been successfully explored for some characteristic examples in pure solvents, analogous investigations for ions in mixed solvents have become of particular interest. Lithium ion in aqueous ammonia represents a very suitable example for such a study, as simulations of Li^+ solutions in water and liquid ammonia have already been carried out using the Born–Oppenheimer *ab initio* QM/MM technique,^{4,6} resulting in a tetrahedral structure with four solvent molecules in the first solvation shell and thus contradicting the octahedral structure predicted for this shell in

both cases on the basis of classical pair potential simulations. An earlier MC simulation of Li^+ in 18.45% aqueous ammonia⁸ based on pair potentials led to a first solvation shell containing four water and two ammonia ligands and a second shell composed of eight water and four ammonia molecules. Although this result is in agreement with qualitative expectations of a preference for the “harder” ligand H_2O over the “soft” NH_3 by the “hard” ion Li^+ , it seemed most worthwhile to examine the correctness of this prediction by the more accurate QM/MM molecular dynamics technique now available.

Methods

The system is partitioned into two regions: the QM/MM molecular dynamics technique treats the ion and its first solvation shell by means of Hartree–Fock level quantum mechanics for the evaluation of forces, whereas the forces between particles inside this region and “outside” solvent particles in the elementary box are computed on the basis of classical pair potentials. Likewise, the forces between molecules in the “outer” region are also treated by molecular mechanics.⁵ The pair potential functions for $\text{Li}(\text{I})$ –water and $\text{Li}(\text{I})$ –ammonia have been obtained previously,^{4,6} and flexible models for intra- and intermolecular interactions were employed for water^{9,10} and ammonia.¹¹ The water–ammonia pair potential was also available from former work.¹² For the quantum mechanically treated region, a double- ζ valence basis set¹³ was used, and long-range interactions were treated by the reaction field procedure.¹⁴

Initially, a classical MD simulation was performed whose equilibrium configuration was used as the starting point for the combined QM/MM simulation. The size of the QM region was selected as a sphere with 3.4 Å diameter, corresponding to the size of the first solvation shell resulting from the classical simulation. Within the interval from 3.4 and 3.6 Å, a smoothing function was applied to ensure a continuous transition between the QM and MM region.

Both simulations were carried out in a canonical ensemble at 293 K with a time step of 0.2 fs. The cubic elementary box with a length of 18.56 Å contained one Li^+ ion, 37 ammonia,

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