

The structure of Co^{2+} in liquid ammonia: Monte Carlo simulation including three-body correction

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Abstract

The solvation structure of Co^{2+} in liquid ammonia was investigated by the Monte Carlo simulation method. The simulation was carried out for a system containing one Co^{2+} and 215 NH_3 molecules with ab initio generated pair and three-body corrected potentials, with the experimental density of pure liquid ammonia at 240 K and 1 atm. of 0.682 g cm^{-3} , corresponding to a periodic cubic of side length 20.86 Å. The results prove the pair potential approximation to fail in predicting correct structural properties of the system. Consideration of the three-body effects reduces the first-shell solvation number of Co^{2+} in liquid ammonia from 8 to 6. The arrangement of ammonia ligands in the first solvation shell shows a rather distorted octahedron with average Co–N distance of 2.24 Å.

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1. Introduction

A metal ion in solution is complexed by some solvent ligands, and knowledge of the solvation structure around the metal ion is very important for the quantitative interpretation of equilibria and kinetic properties of the chemical reactions involving the metal ion [1]. Few experimental methods [2,3] are available for the direct determination of coordination, bond-length and bond-angles for transition metal complexes in solution, although such information is needed for the interpretation of thermodynamic and kinetic data. The most powerful ones from the structural viewpoint are X-ray and neutron diffraction besides spectroscopic techniques such as NMR and quasi-static neutron scattering. These methods, however, quickly reach their limits, in particular for dilute solutions. Sophisticated modelling techniques and structural assumptions required

to interpret experimental data can lead to conflicting results and discrepancies for ionic complex structures, especially for the more labile ions. Additionally, rates of ligand exchange between first and second solvation shell can be so fast that they become inaccessible to experimental measurements and then only mean values of the composition of the metal ion's coordination shell can be derived. These averages can result from a variety of different microspecies present in the solution. The exact composition and distribution of all microspecies can be elucidated, however, by means of computer simulation allowing identification of all distinct microspecies present [4].

Monte Carlo simulations can be effectively used to calculate solvation structures for solutions. By using the assumption of pairwise additive intermolecular potentials and thus neglecting the higher n-body interactions, Monte Carlo simulations for some mono- and divalent metal ions have led to structural results in agreement with those established experimentally [5–7]. In most cases concerning divalent and trivalent ions, however, this simplification of ion–solvent interactions has resulted in overestimated

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