

Ab initio investigation of the structures of NaOH hydrates and their Na⁺ and OH⁻ coordination polyhedra

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ABSTRACT

Plane-wave pseudopotential density functional methods using the Perdew-Burke-Ernzerhof exchange-correlation functional were used to investigate theoretically the structures of five NaOH hydrate phases through optimization of lattice parameters and atomic coordinates. Although all the calculations were carried out with *P1* symmetry, we find in four of the five cases that the experimentally determined space group is maintained to high accuracy. Particular focus is placed on the coordination environments of Na⁺ and OH⁻. The Na-O distances are, in general, overestimated; however, the sodium ion coordination polyhedra are well reproduced by the theoretical calculations, including the fivefold coordinated sodium atom in the α -NaOH·4H₂O structure. The theoretical calculations correctly predict that α -NaOH·4H₂O is lower in energy than the metastable β -NaOH·4H₂O phase; thus, the α phase is stable even in the absence of proton disorder. The octahedral coordination environment around OH⁻ is calculated accurately, including the distances of the weak OH⁻-OH₂ hydrogen bonds in which the hydroxide ion acts as the proton donor. This work provides further evidence of the reliability of the Perdew-Burke-Ernzerhof exchange-correlation functional in hydrogen bonded systems, providing a direct, unambiguous test of the elusive hydroxide-water interaction.