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, underestimated; however, the sodium ion coordination polyhedra are well reproduced by the theoretical calculations, including the fivefold coordinated sodium atom in the \(\alpha\)-NaOH-4H\(_2\)O structure. The theoretical calculations correctly predict that \(\alpha\)-NaOH-4H\(_2\)O is lower in energy than the metastable \(\beta\)-NaOH-4H\(_2\)O phase; thus, the \(\alpha\) 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--OH\(_2\) 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.

INTRODUCTION

Aqueous solutions of sodium salts are common in natural environments in geochemistry and biochemistry, forming electrolytes affecting phenomena such as membrane structure and function and contaminant sorption. They are also important in industrial contexts in corrosion and nuclear waste processing (Yang and Randolph 1999). Although Na\(^+\) is often considered a “background” constituent of the electric double layer, there is increasing evidence that element-specific ion-pair formation may be more important in interfacial chemistry than previously thought (Felmy and Rustad 1998; Wesolowski et al. 2000). Thus, there is motivation to understand the preferred coordination environments of sodium and its influence on neighboring water or other molecules.

For various reasons, the sodium-water interaction is difficult to investigate experimentally (Kameda et al. 1998). The lack of suitable isotopes makes it difficult to isolate the Na-O radial distribution function using neutron diffraction, giving rise to relatively large uncertainties in the hydration number of Na\(^+\) in water (Bruni et al. 2001). Difficulties also arise from the relative weakness of the interaction, and, hence, the diversity of coordination environments in hydrated crystals, and conformational complexity in Na\(^+\)-H\(_2\)O clusters in quantum mechanical studies. Many of these issues have been discussed by White et al. (2000) in their recent first-principles investigation of the hydration of Na\(^+\).

Even more fundamental than the Na\(^+\)-water interaction is the hydroxide-water interaction. The OH\(^-\)-water interaction has been the subject of several ab initio investigations, going back 30 years (Newton and Ehrenson 1971; Tuckerman et al. 1995; Xantheas 1995; Novoa et al. 1997; Pliego and Riveros 2000; Wei et al. 2000). Interest in solvated hydroxide ion is motivated in part by the ion’s fundamental importance in proton transport in aqueous solutions (Geissler et al. 2001). Outside of these theoretical studies, little is known about the solvation of OH\(^-\) in water (Bruni et al. 2001). Investigation of the structures of hydrated hydroxide ions in crystalline phases is one area in which a much-needed connection between experimental data and theoretical calculations can be made. This connection is especially important in that the hydroxide coordination numbers in the gas-phase ab initio studies are much lower than those observed in condensed phases.

Extensive crystallographic investigations of the structures of NaOH\(\cdot\)nH\(_2\)O (Hemily 1953, 1957; Wunderlich 1958; Beurskens and Jeffrey 1964; Seidel 1988; Jacobs and Metzner 1991; Mootz et al. 1994) provide valuable information on the sodium-water and hydroxide-water interaction in well-defined structures. In this paper, we describe computational investigations on the five major NaOH hydrates whose proton positions have been determined: NaOH\(\cdot\)(1, 3.5, 4\(a\), 4\(b\), 7) H\(_2\)O. Because the structural uncertainties associated with the hydrated crystals are much more controlled than those for aqueous species, the structural analysis can proceed with less ambiguity. Hence, the crystalline hydrates serve as an excellent baseline in studies of aqueous solutions (Ojamae et al. 1994). The information presented here serves as a robust foundation for testing various theoretical methods that might be invoked to investigate sodium-water interactions.