American Mineralogist, Volume 84, pages 1641–1649, 1999

Theoretical studies on aluminate and sodium aluminate species in models for aqueous solution: $Al(OH)_3$, $Al(OH)_4^-$, and $NaAl(OH)_4$

J.A. TOSSELL

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, U.S.A.

ABSTRACT

Ab initio quantum mechanical calculations were performed on $Al(OH)_3$, $Al(OH)_4^-$, $NaAl(OH)_4$ and related species with varying numbers of explicit water molecules to elucidate the structural, spectral and energetic properties of the possible species. We find that $Al(OH)_3$ reacts with H_2O in the gas-phase with an exoergicity of 24.1 kcal/mol to produce $Al(OH)_3H_2O$, which has shorter Al-OH distances, larger Al-OH stretching frequencies, and a 15 ppm larger Al NMR shielding than does $Al(OH)_4^-$. When the first hydration spheres of these species are included the Al NMR shieldings becomes very similar, but the O and H NMR parameters and the IR and Raman spectra still show significant differences. The hydration energy of $Al(OH)_3H_2O$ is determined from a “supermolecule” calculation on $Al(OH)_3H_2O...6H_2O$, whereas that for $Al(OH)_4^-$ is obtained using the supermolecule calculation on $Al(OH)_4^-...6H_2O$ plus an evaluation of the electrostatic Born hydration energy of the supermolecule. The calculated energy change for the acid dissociation reaction, $Al(OH)_3H_2O...6H_2O \rightarrow Al(OH)_4^-..6H_2O + H^+$, is +297.9 kcal/mol in the gas phase but only +2.3 kcal/mol in aqueous solution, due to the strong hydration of H^+ and $Al(OH)_4^-..6H_2O$. Using quantum mechanically calculated entropies for the unhydrated species, $Al(OH)_3H_2O$ and $Al(OH)_4^-$, plus the experimental hydration entropy of H^+, the $-T\Delta S$ term for this reaction is calculated as about +11.8 kcal/mol. Adding in calculated zero-point energies and room temperature enthalpy corrections gives a free energy change of +0.5 kcal/mol. Thus pKa for the acid dissociation of $Al(OH)_3H_2O$ is near zero at room T, and $Al(OH)_4^-$ will be dominant except under very acidic conditions.

Properties are also calculated for the bare close-contact ion pair $NaAl(OH)_4$ and for hydrated forms of both a close-contact and a solvent-separated ion pair, $NaAl(OH)_4...10H_2O$ and $NaAl(OH)_4...11H_2O$. In accord with previous calculations on silicate anions and ion pairs, formation of an unhydrated close-contact ion pair increases the shielding of the Al in $Al(OH)_4^-$, while reducing the Al-O symmetric stretching frequency. The calculated energy change at 298 K in aqueous solution for the ion pair formation reaction,

$$Na...6H_2O^+ + Al(OH)_4^-..6H_2O \rightarrow NaAl(OH)_4...11H_2O + H_2O,$$

is +17.6 kcal/mol, close to the value determined experimentally. After addition of calculated zero-point energies, enthalpy corrections, and calculated entropy changes we obtain a ΔG value of +1.7 kcal/mol for this reaction, giving a log K around –1, consistent with significant ion pair formation. The $NaAl(OH)_4...11H_2O$ species is a solvent-separated ion pair with full hydration of both its Na^+ and $Al(OH)_4^-$. Its calculated Al NMR shielding and Al-O symmetric stretching frequencies are very similar to those for $Al(OH)_4^-...6\,H_2O$, whereas its Na NMR shielding is about 5 ppm smaller than that of $Na(OH_2)_6^+$, although its Na electric field gradient (and consequently its line-width) are larger. Thus it appears that Na NMR may be the best technique for characterizing this ion pair.