Theoretical studies on aluminite and sodium aluminite 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$_2$O in the gas-phase with an exoergicity of 24.1 kcal/mol to produce Al(OH)$_3$H$_2$O, which has shorter Al-OH distances, larger Al-OH stretching frequencies, and a 15 ppm larger Al NMR shielding than does Al(OH)$_3^-$.

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 calculated energy change for the acid dissociation reaction, Al(OH)$_3$H$_2$O...6H$_2$O $\rightarrow$ Al(OH)$_3^-...6$H$_2$O $+$ 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)$_3^-...6$H$_2$O. Using quantum mechanically calculated entropies for the unhydrated species, Al(OH)$_3$H$_2$O and Al(OH)$_3^-$, 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)$_3$H$_2$O is near zero at room T, and Al(OH)$_3^-$ 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)$_4^-...10$H$_2$O and NaAl(OH)$_4^-...11$H$_2$O. 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)$_3^-$, while reducing the Al-O symmetric stretching frequency. The calculated energy change at 298 K in aqueous solution for the ion pair formation reaction,

$$\text{Na}...6\text{H}_2\text{O}^+ + \text{Al(OH)}_3^-...6\text{H}_2\text{O} \rightarrow \text{NaAl(OH)}_4^-...11\text{H}_2\text{O} + \text{H}_2\text{O},$$

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 $\Delta G$ value of +1.7 kcal/mol for this reaction, giving a log K around –1, consistent with significant ion pair formation. The NaAl(OH)$_4^-...11$H$_2$O species is a solvent-separated ion pair with full hydration of both its Na$^+$ and Al(OH)$_3^-$. Its calculated Al NMR shielding and Al-O symmetric stretching frequencies are very similar to those for Al(OH)$_3^-...6$H$_2$O, whereas its Na NMR shielding is about 5 ppm smaller than that of Na(OH)$_2$,$^+$, 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.

INTRODUCTION

As discussed by Walther (1997), understanding the extent of mass transfer between minerals and fluids in the Earth’s crust...requires knowing the solubility of minerals. For aluminosilicate solubilities in particular we must determine the stoichiometry and stability of a potentially large number of aqueous Al-containing species. Traditionally, this has been done through solubility studies (Martell 1992; Castet et al. 1993; Wesolowski and Palmer 1994), i.e., by measuring the total amount of Al in solution as a function of pH, temperature, pressure, and the concentrations of other ions, e.g., Cl$^-$. If a set of complex ion species is then assumed, their formation constants can be least squares fitted to the measured solubility data. However, there are several problems with this procedure: (1) the necessary experiments are time consuming and the metal concentrations may be both difficult to determine and strongly dependent on experimental conditions, e.g., upon the precise form of the mineral considered, (2) different sets of complexes may describe the data equally well and yet may produce widely differing values of the formation constants, and (3) the partici-