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

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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,

$$Na...6H_2O^+ + Al(OH)_4^-..6H_2O \rightarrow NaAl(OH)_4...11H_2O + H_2O,$$
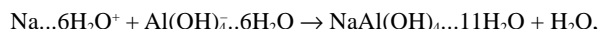
is +17.6 kcal/mol, close to the value determined experimentally. After addition of calculated zero-point energies, enthalpy corrections, and calculated entropy changes we obtain a ΔG value of +1.7 kcal/mol for this reaction, giving a log K around –1, consistent with significant ion pair formation. The $NaAl(OH)_4...11H_2O$ 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.
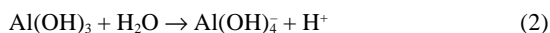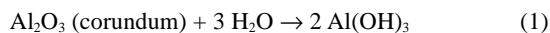
INTRODUCTION

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-

pation of a chemical component in the species cannot be determined if its activity cannot be varied. For example, we cannot determine how H_2O participates in species formed in dilute aqueous solution from solubility data alone and we cannot generally distinguish monomeric metal-containing species from oligomers since we cannot vary the activity of the pure mineral component. These sources of ambiguity have created substantial controversy concerning the Al-containing species present when corundum or other Al oxide and oxyhydroxide minerals dissolve in water, under various conditions. The basic equations to be considered, e.g., for the case of corundum in NaOH or NaCl aqueous solution are:

$$Al_2O_3 \text{ (corundum)} + 3 H_2O \rightarrow 2 Al(OH)_3 \qquad (1)$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \qquad (2)$$

$$Al(OH)_4^- + Na^+ \rightarrow NaAl(OH)_4. \qquad (3)$$

Depending upon the value used for the equilibrium constant of Equation 2 the predominant species present when corundum dissolves in water near neutral pH may be either $Al(OH)_3$ or $Al(OH)_4^-$. In the same way, the increased solubility of Al_2O_3 in NaOH solution can be explained entirely in terms of the contribution of $Al(OH)_4^-$ using certain values for this equilibrium constant, whereas lower values for the equilibrium constant of Equation 2 require contributions from the $NaAl(OH)_4$ species of Equation 3 to match the experimental solubilities. For example, Pokrovskii and Helgeson (1995) indicated a substantial stability for species like $NaAl(OH)_4$, whereas Anderson (1995) notes that such a species need not be invoked if the formation constant for $Al(OH)_4^-$ is chosen appropriately and Walther (1997) excludes species such as $NaAl(OH)_4$ from consideration, based partly on entropic arguments more appropriate to a gas phase reaction. Of course, the controversy involves not just ambient measurements but the characteristics of such reactions at elevated T and P in hydrothermal systems. Neutral species are expected to be favored at high T because of the decrease in the dielectric constant of water (Uematsu and Franck 1980) and because their formation from ions generally reduces the degree of order of the solvent and thus increases the overall entropy of the system (Marcus 1986). This paper is restricted to relatively low temperatures, from $T = 0$ K to $T = 298$ K.

Unfortunately Equation 1 is very difficult to treat using quantum mechanical theory, because the methods used for describing the electronic structures of crystalline solids, such as corundum, are substantially different in detail from those used to describe the electronic structure of a molecule such as $Al(OH)_3$. It is therefore difficult to avoid mathematical artifacts in comparing the total energies of corundum and $Al(OH)_3$. Methods which treat the different phases alike, e.g., those utilizing a common force field, avoid this problem but their results are strongly dependent upon the force field parameterization and may not contribute much to a fundamental understanding of the problem. Equations 2 and 3 are much more amenable to quantum mechanical calculations. We can evaluate reaction energetics first for gas-phase forms of the species and then add corrections for hydration. However, that the methods for making such correc-

tions are still relatively crude and that including all the physical effects (and including each only once) can be quite difficult.

There is also the more fundamental question of relating quantities evaluated on a microscopic scale through quantum mechanics and quantum statistical mechanics with those determined macroscopically through experimental thermodynamics. For example, Pokrovskii and Helgeson (1995) noted that according to standard thermodynamic conventions AlO_2^- and $Al(OH)_4^-$ are the same—i.e., differences in all the thermodynamic quantities for the reaction:

$$AlO_2^- + 2 H_2O \rightarrow Al(OH)_4^- \qquad (4)$$
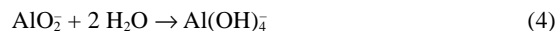
are defined to be zero, whereas the change in internal energy calculated quantum mechanically for this reaction in the gas phase is -144 kcal/mol.

In many cases, additional constraints can be placed upon the identity and structure of the complexes present by examining structural data, e.g., from extended X-ray absorption fine structure (EXAFS) or spectral data, e.g., infrared, Raman or NMR spectroscopies. For example, we have used these procedures to determine the speciation of As in sulfidic solutions (Helz et al. 1995).

For many Al-containing minerals, the solubilities are so low (at least for most conditions of pH, T, P, etc.) that spectral data for the solution species are not presently available. It could also be the case that some types of spectra would not adequately distinguish between the different species. In determining speciation of Al-containing species in glasses EXAFS, IR, Raman, and NMR spectroscopy have all proven valuable (Stebbins et al. 1995). To help assess speciation of Al-containing complexes in solution it would therefore be useful to determine Al-O distances, IR and Raman frequencies, and Al, Na, O, and H NMR shieldings, and nuclear quadrupole coupling constants. Eremin et al. (1974) has summarized experimental data on aluminate ions in solution which has been interpreted in terms of alkali-aluminate ion pairs, but in all the cases considered the small spectral changes have been attributed to ioin pair formation without any supporting calculation of what the properties of the ion-pair actually are. In addition to the calculation of properties we can directly calculate the energetics for formation of the various species in aqueous solution. This work calculates structures, spectra, and stabilities for a range of Al- and Na-containing species, both "bare" and with an approximate representation of their first hydration spheres.

COMPUTATIONAL METHODS

Modern quantum chemical methods are able to reproduce reaction energies to chemical accuracy (1–2 kcal/mol) for small molecules composed of light atoms in the gas phase (Hehre et al. 1986; Foresman and Frisch 1996). Evaluating the energetics of reactions in solution is much more difficult, but is a current focus of interest in quantum chemistry. The basic procedure for gas-phase reactions is to solve an approximate version of the Schrodinger equation, typically the Hartree-Fock or the Kohn-Sham equations, to reasonable accuracy (Foresman and Frisch 1996). A general problem is that mean-field procedures

such as the Hartree-Fock, in which the instantaneous electron-electron repulsion is replaced by an averaged value, can give serious errors in energies unless the reaction is of a specific, limited "isodesmic" type. Corrections for the "correlation" error must generally be made to get accurate energies. A computationally efficient correction method is second order Moller-Plesett perturbation theory (MP2). We can treat even very heavy atoms such as Hg, for which relativistic effects are important, by using relativistic effective core potentials and an orbital basis set which treats only the valence electrons explicitly (e.g., Stevens et al. 1992; the SBK basis set). Even for third row atoms such as Al the use of effective core potentials and valence only basis sets greatly reduces the amount of computation required, with very little decrease in accuracy of result for geometries and relative stabilities. We can also calculate vibrational spectra for such gas-phase systems and evaluate zero-point vibrational energies and finite temperature translational, vibrational, and rotational contributions to the energy, enthalpy, and entropy.

Our calculations of equilibrium structures, energies, vibrational frequencies, and electric field gradients were done primarily with the GAMESS quantum chemical software (Schmidt et al. 1993) whereas the calculations of NMR shieldings were done using the GIAO (gauge-including atomic orbital method; Hinton et al. 1993) incorporated in the quantum chemical software GAUSSIAN94 (Frisch et al. 1994). Both programs utilize conventional Hartree-Fock self-consistent-field molecular orbital theory, as described, e.g., in Hehre et al. (1986). Unfortunately, for some of the larger hydrated structures, such as $NaAl(OH)_4...11H_2O$, we have been unable to obtain energy convergence to the accuracy needed to reliably evaluate zero-point energies and vibrational entropies, invariably finding some negative vibrational frequencies indicating that we are at a saddle point with respect to the orientation of some of the water molecules. We have calculated the higher vibrational frequences for these systems, corresponding to Al-O stretching vibrations, and consider them to be reliable. Analysis of zero-point energy, enthalpy, and entropy terms are therefore done using the unhydrated species, for which the vibrational calculations yield all positive frequencies.

For solution reactions a serious problem is the representation of the interaction of the solute with the solvent. There are several general schemes for evaluating the solution energies, including (1) polarizable continuum models, such as the self-consistent reaction field (SCRF) model, in which the energy change due to polarization of the bulk solvent by the charge distribution of the solute is evaluated (e.g., Wiberg et al. 1996) (2) supermolecule approachs, in which the solute and several explicit solvent molecules surrounding it are treated quantum mechanically, and (3) simulation techniques, in which many solvent molecules interact with the solute through pair or high order potentials, calculated quantum mechanically or fitted to experiment. We have previously used polarizable continuum and supermolecule approachs to study the properties of arsenic hydroxide species in solution (Tossell 1997). Here we use primarily a supermolecule approach, although we have calculated SCRF energies for some of the supermolecule ions. Born energies for the supermolecule ions are evaluated using the Rashin

and Honig (1985) reformulaton of Born theory. The only quantity (aside from the dielectric constant of the solvent) needed to evaluate the Born energy is the Born radius, which unfortunately is an ambiguous quantity. In the Rashin and Honig (1985) formulation the Born radius for a species like $Al(OH)_4^-...6H_2O$ is the (average) distance from the central Al to the O of the first hydration sphere water molecules plus the "OH" radius, chosen as 1.498 Å in Rashin and Honig (1985). The choice of hydration enthalpy for the proton is a difficult one. The best modern experimental value is probably –275 kcal/mol (Coe 1994), although this value is obtained by extrapolation of cluster experimental data. The best calculated value is about –267.3 kcal/mol (Tawa et al. 1998) and was obtained with an approach similar to that used in this work, namely quantum mechanical calculations (at a higher level than used here) upon H^+ containing supermolecules (with 1–6 water molecules) embedded in a polarizable continuum. We therefore chose the Tawa et al. (1998) value for the proton hydration enthalpy. Although the experimental and calculated values mentioned above are quite similar, the particular choice of proton hydration enthalpy strongly influences the overall enthalpy of reaction 2, the $Al(OH)_3$, $Al(OH)_4^-$ equilibrium.

Although there have been no recent quantum mechanical studies on exactly the aluminate systems considered here, a very relevant recent work is that by Moravetski et al. (1996), who considered the ^{29}Si NMR shieldings of the species $Si(OH)_4$ [isoelectronic to $Al(OH)_4^-$] and its anion $Si(OH)_3O^-$, interacting with H_2O and with K^+. An important conclusion was that the Si in the $Si(OH)_3^-$ anion was shielded to a moderate degree by the addition of either water or K^+ whereas the addition of water to neutral $Si(OH)_4$ had a much smaller effect on the Si shielding. We see similar trends for the aluminates, as will be shown below.

RESULTS

Geometries

In Figure 1 we show equilibrium geometries calculated at the Hartree-Fock SCF level using a polarized SBK basis set (single d polarization functions on all the atoms except H) for the various species considered. Relevant Al-O distances are in Table 1. We clearly reproduce the expected difference in Al-O distance between $Al(OH_2)_6^{3+}$ and $Al(OH)_4^-$. We also find that the Al-O distances are smaller in $Al(OH)_3$ than in $Al(OH)_4^-$ and that the distances to the –OH and –OH$_2$ atoms are quite different in $Al(OH)_3H_2O$. This difference is little changed if we perform a polarized continuum calculation on $Al(OH)_3H_2O$ using the SCRF approach or explicitly model its first hydration sphere using a $Al(OH)_3H_2O...6H_2O$ supermolecule (Table 1). Likewise coordinating six water molecules to $Al(OH)_4^-$ causes only a slight inequivalence of the Al-O distances and the average distance is changed by <0.01 Å. However, in $NaAl(OH)_4$ the distances from Al to the –OH coordinated to Na are significantly increased, whereas the other two Al-O distances decrease. When water molecules are then added to $NaAl(OH)_4$ the inequivalence of the Al-O distances is reduced. Note that $NaAl(OH)_4$ is a "bare" contact ion pair, whereas $NaAl(OH)_4..10H_2O$ and $NaAl(OH)_4...11H_2O$ are, respectively, fully hydrated contact and solvent separated ion pairs. By fully hydrated, we mean that

both Na^+ and $Al(OH)_4^-$ have six nearest neighbor groups, either H_2O or each other. $NaAl(OH)_4...H_2O$ is a close contact ion pair in which the H_2O is coordinated to Na^+. We tested several geometries for this molecule, with H_2O coordinated to Na^+, $Al(OH)_4^-$, or to both groups, and the geometry in which H_2O binds to Na^+ was found to be the most stable. We found the same type of geometry for $NaClO_4...H_2O$.
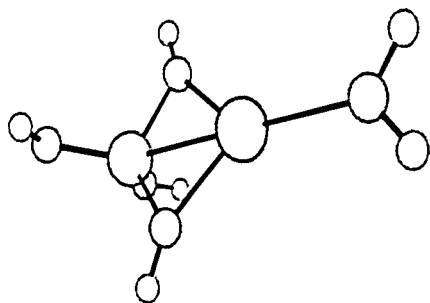
NaAl(OH)4...H2O
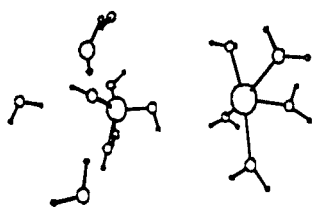
NaAl(OH)4...10H2O
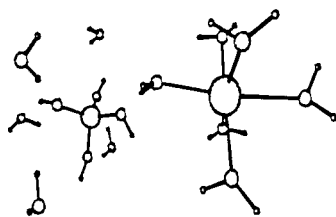
NaAl(OH)4...11H2O

FIGURE 1. Equilibrium geometries calculated at the polarized SBK SCF level for various species. Atoms in order of decreasing size are Al, Na, O, and H.

NMR shieldings

Table 2 shows that we satisfactorily reproduce the difference in shielding between $Al(OH_2)_6^{3+}$ and $Al(OH)_4^-$. Experimentally, the shielding difference in solution is just about 80 ppm, with the $Al(OH)_4^-$ deshielded (Akitt and Gessner 1984), so that it appears at $\delta = +80$ ppm compared to the $Al(OH_2)_6^{3+}$ (or $AlCl_3$, aqueous) reference. For the bare ions $Al(OH_2)_6^{3+}$ and $Al(OH)_4^-$, optimized at the polarized SBK level and using the GIAO method with 6-31G* basis sets, we calculate a shielding difference of about 88 ppm. If we add in the Born energy the equilbrium distance for each ion will decrease, since a smaller species will have a larger Born stabilization. This effect is much larger for $Al(OH_2)_6^{3+}$ than for $Al(OH)_4^-$, partly because of its larger charge magnitude and partly because of its smaller Al-O stretching force constants. For $Al(OH_2)_6^{3+}$ including the Born term reduces the equilibrium bond distance to 1.876 Å (from 1.927 Å for the free ion) whereas in $Al(OH)_4^-$ the change is only from 1.767 to 1.760 Å. The experimental value for the Al-O distance in $Al(OH_2)_6^{3+}$ is usually quoted as 1.87–1.90 Å (Marcus 1988). Using an Al-O distance of 1.876 Å for $Al(OH_2)_6^{3+}$ the ^{27}Al NMR shielding difference of the two ions drops to about 84 ppm. These results are discussed more completely in Tossell (1998). Sykes et al. (1997) have reported similar results for the

TABLE 1. Calculated Al-O nearest-neighbor distances (in angstrom) obtained using polarized SBK bases for various Al-containing species

Molecule	R(Al-O)
$Al(OH_2)_6^{3+}$	1.927 × 6 (1.876 × 6*)
$Al(OH)_3$	1.683 × 3
$Al(OH)_3H_2O$	1.709, 1.720, 1.724, 1.977
	(1.718, 1.720, 1.726, 1.981*)
$Al(OH)_3H_2O...6H_2O$	1.706, 1.710, 1.738, 1.975
$Al(OH)_4^-$	1.767 × 4
$Al(OH)_4^-..6H_2O$	1.760, 1.762, 1.765, 1.768
$NaAl(OH)_4$	1.722 × 2, 1.808 × 2
$NaAl(OH)_4...H_2O$	1.725 × 2, 1.802 × 2
$NaAl(OH)_4...10H_2O$	1.754, 1.763. 1.774, 1.784
$NaAl(OH)_4...11H_2O$	1.748, 1.748, 1.778, 1.793

* Value obtained when Born term is included in the total energy.
† Values obtained from SCRF calculation.

TABLE 2. Al and Na NMR shieldings (in parts per million)

Molecule	σ^{Al}	σ^{Na}
bare Al^{3+}	765.8	
$Al(OH_2)_6^{3+}$	636.4 (637.3*, 632.2†)	
$Al(OH)_3$	543.2	
$Al(OH)_3H_2O$	562.7	
$Al(OH)_3H_2O...6H_2O$	558.6 (555.9‡)	
$Al(OH)_4^-$	548.1	
$Al(OH)_4^-...6H_2O$	559.6 (557.3‡)	
$Al(OH)_3O^{2-}$	540.5	
$(OH)_3AlOAl(OH)_3^{2-}$	554.8	
Na^+ (gas-phase)		623.2
$Na(OH_2)_6^+$		588.9
$NaAl(OH)_4$	557.5	590.3
$NaAl(OH)_3O^-$	547.7	578.7
$NaAl(OH)_4..H_2O$	556.0	583.1
$NaAl(OH)_4..10H_2O$	557.5	590.6
$NaAl(OH)_4..11H_2O$	559.2	583.9

Notes: Calculated using the 6-31G* basis set, the GIAO method and polarized SBK optimized geometries.
* 6-31G* optimum geometry.
† Polarized SBK SCF + Born energy equilibrium geometry.
‡ At hydrated geometry, but with extra six water molecules removed.

Al NMR shieldings of $Al(OH_2)_6^{3+}$ and $Al(OH)_4^-$. The deshielding of Al in these various species (relative to free Al^{3+}) depends upon both the identities of the O-containing ligands and the Al-O distances. The deshielding per ligand is essentially a linear function of $R(Al-O)^-$, for both the –OH and $–OH_2$ ligands. For example, based on our calculated shieldings as a function of R(Al-O) for $Al(OH)_4^-$ and $Al(OH_2)_6^{3+}$, we can predict the shielding of $Al(OH)_3H_2O$ to within about 10 ppm.

The ^{27}Al shielding also depends upon the degree of polymerization. For example, the aluminate dimer $(OH)_3AlOAl(OH)_3^{2-}$ is calculated to be shielded compared to the $Al(OH)_4^-$ monomer by 6.7 ppm. The calculated structure for this dimer is similar to that observed by Kaduk et al. (1995) in crystalline sodium aluminates. Such increased shielding upon polymerization has been repeatedly observed for Al, Si, and P (among others). The ^{27}Al NMR signal observed near $\delta = 70$ ppm by Akitt and Gessner (1984) presumably arises from such a polymeric species, although not necessarily from one as simple as $(OH)_3AlOAl(OH)_3^{2-}$.

When H_2O or Na^+ interacts with $Al(OH)_4^-$ the Al shielding is increased, just as seen by Moravetski et al. (1996) for the addition of H_2O or K^+ to the $Si(OH)_3O^-$ anion. For example, $Al(OH)_4^-...6H_2O$ is shielded by 11.5 ppm and $NaAl(OH)_4^-$ by 9.4 ppm, compared to $Al(OH)_4^-$. The alkali metal cation results are at first surprising, because introduction of alkali metal oxides to SiO_2 produces species that are deshielded compared to the parent SiO_2. It is often suggested that association with electropositive atoms such as Na must deshield the other atoms, so that Al in the $NaAl(OH)_4$ ion-pair would be deshielded with respect to $Al(OH)_4^-$. However, this is certainly not the case. The deshielding of Si produced by alkali oxides added to SiO_2 is essentially a consequence of the depolymerization those oxides cause, not the close approach of Na^+ to the Si.

However, the effect of $Na(H_2O)_{6+}$ addition is very small when the $Al(OH)_4^-$ species is already fully hydrated, e.g., $NaAl(OH)_4...11H_2O$ and $Al(OH)_4^-...6H_2O$ differ in Al shielding by only 0.4 ppm, with the ion-pair deshielded. Hence, it would be difficult to distinguish these two species on the basis of Al NMR shieldings alone, given that ^{27}Al is a quadrupolar nuclide and consequently often has large linewidths. By contrast, for $NaClO_4$ solutions the NMR shielding of ^{35}Cl (also a quadrupolar nuclide) is observed to decrease by only a fraction of a part per million as the concentration is increased (Miller et al. 1985), but the effect can be seen because the line widths remain small due to the rigidity of the ClO_4 unit. This deshielding has been attributed to ion pair formation. The same effect may be observable for the $NaAl(OH)_4...11H_2O$ species if the nuclear quadrupole coupling constant is small enough, and the calculations reported in Table 3 indicate that it increases by only about a factor of 2 from $Al(OH)_4^-...6H_2O$ to $NaAl(OH)_4^-...6H_2O$.

Likewise $Al(OH)_3H_2O...6H_2O$ and $Al(OH)_4^-...6H_2O$ have very similar Al shieldings, differing by only 1 ppm, although the unhydrated species, $Al(OH)_3H_2O$ and $Al(OH)_4^-$ show a substantial shielding difference. The effect of adding six water molecules to $Al(OH)_3H_2O$ is to slightly lower the Al shielding, whereas the addition of six water molecules to $Al(OH)_4^-$ increases the shielding significantly, so that the hexahydrated species have very similar shieldings. These results are only slightly changed if we omit the six added water molecules from

the NMR shielding calculation and consider only the $Al(OH)_3H_2O$ and $Al(OH)_4^-$ species, but at the geometries they would have in the presence of the six water molecules. Therefore, it is mainly the effect of these six water molecules on the local geometries of $Al(OH)_3H_2O$ and $Al(OH)_4^-$ that is responsible for the changes in Al shielding. The changes in Na shielding are a bit more diagnostic. The three species with Na in basically sixfold coordination, $Na(OH_2)_6^+$, $NaAl(OH)_4...10H_2O$, and $NaAl(OH)_4...11H_2O$ show substantially different shieldings, with the Na in the solvent separated ion pair deshielded by about 5 ppm compared to $Na(OH_2)_6^+$.

There may also be some diagnostic value in the ^{17}O and ^1H NMR shieldings of the $Al(OH)_3H_2O$ and $Al(OH)_4^-$ species and their hexahydrates. Assuming slow exchange of the OH^- and H_2O groups of $Al(OH)_3H_2O$ with solution and a rapid exchange of protons between these ligands themselves, we should see ^{17}O and ^1H NMR signals averaged over the first coordination sphere OH^- and H_2O. The average ^{17}O NMR shieldings for $Al(OH)_3H_2O$ and $Al(OH)_4^-$ are 326.0 and 322.0 ppm, respectively, whereas the average ^1H shieldings are 31.0 and 34.1 ppm, respectively. In the hexahydrated species the ^{17}O and ^1H shieldings are all a couple parts per million lower, but the difference between the $Al(OH)_3H_2O...$ and $Al(OH)_4^-...$ species remains about the same. In the hydrolysis of $Be^{+2}(aq)$ a series of ^1H NMR peaks have indeed been observed corresponding to different types of hydrolyzed species (Akitt and Duncan 1980).

Electric field gradients

The NQCC value (e^2qQ/h) for $Al(OH)_4^-$ is not zero (Table 3) since the equilibrium geometry of this species is S_4, not T_d. Its calculated NQCC value of 2.2 is unaffected by solvation with six water molecules. The NQCC is much larger (19.5 MHz) for $Al(OH)_3H_2O$ and remains large even in the presence of six water molecules of hydration. In the bare ion-pair $NaAl(OH)_4$ the Al NQCC is quite large but it is smaller in the partly and fully solvated versions of both the contact and solvent-separated ion-pairs. Still the Al NQCC is about twice as large in the fully hydrated $NaAl(OH)_4$ ion pairs as it is in fully hydrated $Al(OH)_4^-$. Thus the effect of ion pair formation would be seen in the Al NQCC and consequently the Al NMR linewidth (which would also be increased by the presence of multiple exchanging species).

TABLE 3. Calculated electric field gradients* and nuclear quadrupole coupling constants†

Molecule	q_{Al}	$e^2q_{Al}Q_{Al}/h$	q_{Na}	$e^2q_{Na}Q_{Na}/h$
$Al(OH)_3$	0.8550	25.7		
$Al(OH)_3H_2O$	0.6373	19.2		
$Al(OH)_3H_2O..6H_2O$	0.6489	19.5		
$Al(OH)_4^-$	0.0728	2.2		
$Al(OH)_4^-...6H_2O$	0.0742	2.2		
$Na(OH_2)_6^+$			0.0211	0.4
$NaAl(OH)_4$	0.2893	8.7	0.1629	3.3
$NaAl(OH)_3O^-$	0.1288	3.9	0.3138	6.3
$NaAl(OH)_4..H_2O$	0.2684	8.1	0.1864	3.7
$NaAl(OH)_4.. 10H_2O$	0.1183	3.6	0.0758	1.5
$NaAl(OH)_4...11H_2O$	0.1505	4.5	0.0391	0.8

* In Au, evaluated at polarized SBK optimized geometries using 6-31G* basis sets.
† In MHz, assuming $eQ_{Al}=1.5 \times 10^{-1}$ barns and $eQ_{Na}=1.0 \times 10^{-1}$ barns for Al and Na complexes.

Vibrational spectra

It is worthwhile to examine the IR and Raman frequencies of such species, to determine what effect ion pairing might have. In Table 4 we show stretching frequencies for AlF_4^-, ClO_4^-, and $Al(OH)_4^-$, and some larger aluminate species. It is useful to consider results for ClO_4^- and species formed from it because the pairing of this ion with alkali metal cations has been studied both in matrix isolation and in aqueous solution. We first observe that the calculated symmetric stretching frequencies are somewhat smaller than experiment, but not by the 0.893 factor

often observed for neutral gas-phase molecule (Pople et al. 1993). In general, the unbalanced negative charge on an anion will tend to increase its bond distances and decrease its force constants, so that stretching frequencies are not exaggerated to the extent found for neutrals. For $Al(OH)_4^-$ in aqueous solution Moolenaar et al. (1970) have used infrared and Raman spectroscopy to characterize an antisymmetric Al-O bending mode at about 325 cm^{-1}, the Al-O symmetric stretch at 625 cm^{-1} and the Al-O antisymmetric stretch at 725 cm^{-1}. Figure 2 shows the calculated normal modes of $Al(OH)_4^-$. Based on these plots the

TABLE 4. Calculated (unscaled) and experimental values for Al-F, Cl-O and Al-O symmetric and antisymmetric stretching frequencies (in cm^{-1})

Molecule	Calculated		Experimental	
	Symmetric	Antisymetric	Symmetric	Antisymetric
AlF_4^-	630	815	622	760*
ClO_4^-	948	1146	919b†	1112†
$NaClO_4$	941	1062, 1168, 1232	905†	1011, 1128, 1190‡
$NaClO_4..H_2O$	943	1072, 1167, 1226		
$Al(OH)_4^-$	616	720, 733, 733	625‡	725‡
$Al(OH)_4^-...6H_2O$	633	750, 768, 814		
$NaAl(OH)_4$	610	654, 665, 780		
$NaAl(OH)_4..H_2O$	613	667, 673, 778		
$Al(OH)_3H_2O$	438§	765, 900, 912		
$Al(OH)_3H_2O...6H_2O$	434§	697, 844, 868		
$NaAl(OH)_4...11H_2O$	629	747, 765, 796		

* Gilbert et al. (1974).
† Draeger et al. (1979).
‡ Moolenaar et al. (1979).
§ Al-OH$_2$ stretching mode.

Al(OH)3H2O
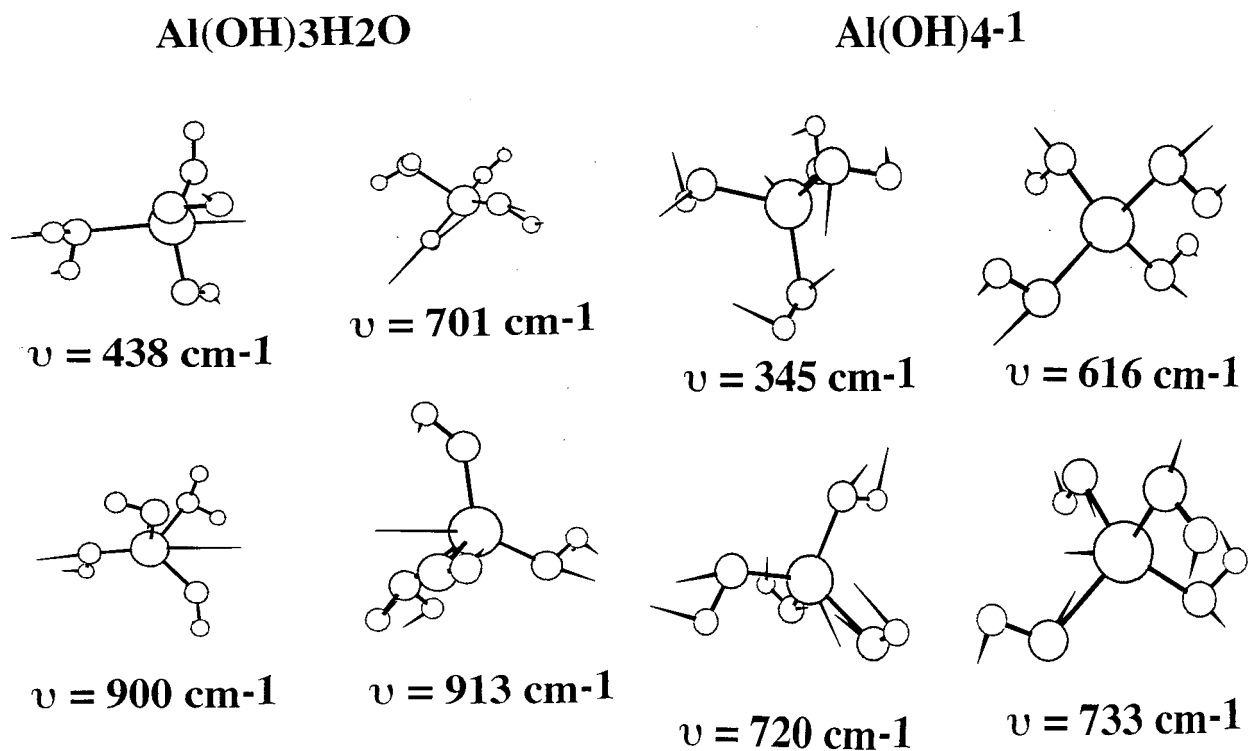
Al(OH)4-1

$\upsilon = 438$ cm-1

$\upsilon = 701$ cm-1

$\upsilon = 345$ cm-1

$\upsilon = 616$ cm-1

$\upsilon = 900$ cm-1

$\upsilon = 913$ cm-1

$\upsilon = 720$ cm-1

$\upsilon = 733$ cm-1

FIGURE 2. Calculated normal modes of vibration for $Al(OH)_4^-$ and $Al(OH)_3H_2O$. Atoms as in Figure 1. Directions and magnitudes of arrow indicate nuclear motion within the normal modes. Calculated frequencies are given along with the normal modes.

345 (e symmetry) and 616 (a symmetry) modes certainly correspond to Al-O antisymmetric bending and Al-O symmetric stretching, respectively, whereas the Al-O antisymmetric stretching mode is split in S_4 symmetry into the two components at 720 (b symmetry) and 733 cm^{-1} (e symmetry). For the hexahydrated species $Al(OH)_4^-...6H_2O$ both the symmetric and antisymmetric Al-O stretching frequencies are increased by 20 to 70 cm^-, although the form of the normal modes is little changed. For $Al(OH)_3H_2O$ the vibrational frequencies are significantly different. There is now a low energy Al-OH$_2$ stretching vibratition (438 cm^{-1} in the unhydrated species) and the three Al-OH stretching frequencies are higher in energy than in $Al(OH)_4^-$, due to the shorter Al-O distances. For the hexahydrated species $Al(OH)_3H_2O…6H_2O$ the Al-O stretching frequencies are reduced by around 50 cm^{-1}, but they are still higher in energy than those for $Al(OH)_4^-...6H_2O$. This suggests that the $Al(OH)_4^-$ and $Al(OH)_3H_2O$ species can be distinguished by IR and Raman spectroscopy.

For a T_d symmetry species like AlF_4^- or ClO_4^-, the a_1 mode is only Raman active, whereas the e and t_2 modes are both Raman and IR active. For S_4 symmetry $Al(OH)_4^-$ the a mode is only Raman active whereas b and e are both Raman and IR active. In practice, the Raman spectrum of aqueous $Al(OH)_4^-$ is dominated by the symmetric stretching peak observed at 625 cm^{-1} whereas the IR spectrum is dominated by a broad antisymmetric stretching peak with a maximum around 725 cm^{-1} and with extra intensity on the high frequency side. For very high Al concentrations additional peaks appear in both the Raman and IR spectra, but we find no features at these new frequencies in the calculated spectra of $Al(OH)_4^-...6H_2O$ or $NaAl(OH)_4$ $...11H_2O$. For the dimer $Al_2O(OH)_6^{2-}$ there are symmetric and antisymmetric stretchs of the Al-O$_{bridging}$ bonds which are calculated to occur between 900 and 1000 cm^{-1}, which may correspond to the feature near 900 cm^{-1} in the high Al concentration experimental spectrum.

Draeger et al. (1979) studied the IR spectra of $MClO_4$ ion pairs in inert gas matrices with differing amounts of water added. The found that the a_1 symmetry symmetric stretching vibration of ClO_4^- was lowered in the bare ion pairs but increased again when water was added to the system. However, most of their attention was devoted to the splitting of the Cl-O antisymmetric t_2 stretching mode, which was quite large in the bare ion pairs but dropped quickly upon water addition. It is clear from their results that the magnitude of perturbation of ClO_4^- produced by the Na^+ cation is strongly dependent upon the water content, and thus upon the degree of hydration of the ion pair. This is consistent with the results shown in Table 4 for ClO_4^-, $NaClO_4$, and $NaClO_4...H_2O$ and for the analogous $Al(OH)_4^-$ species. Miller and Macklin (1985) studied Na^+-ClO_4^- ion-pair formation in aqueous solution. They found that the splitting of the asymmetric t_2 vibration was so small that it gave no information on ion pairing. This certainly indicated that the ion-pair was highly hydrated. They did however resolve the symmetric a_1 stretching band into three components at 933, 938, and 942 cm^{-1}, which they attributed to hydrated ClO_4^-, a solvent-separated $NaClO_4$ ion pair and a contact ion pair, respectively. It is difficult to reconcile their results with our calculations on $Al(OH)_4^-...6H_2O$ and $NaAl(OH)_4...11H_2O$, which

show the ion pair to have a lower symmetric stretching frequency (although admittedly we have not done the analogous calculations on the $NaClO_4$ system). In any case, it appears that in aqueous solution the effect of ion pairing on the vibrational spectrum of ClO_4^- is small compared to the solution line widths and the assignments of the various species are uncertain. Our calculations indicate that both the symmetric and antisymmetric Al-O stretching frequences will decrease slightly from $Al(OH)_4^-...6H_2O$ to $NaAl(OH)_4...11H_2O$. It is not clear whether this effect would be observable, given the width of the spectral features.

Energetics

We now examine the energetics for the various species. First, we find that using our supermolecule approach only those species with a complete stable nearest-neighbor coordination sphere about the Al^{3+} cation are well defined. For example, in reaction 1 shown in Table 5 we consider the addition of two molecules of water to the twofold-coordinated species AlO_2^- to give $Al(OH)_4^-$. In the gas-phase this reaction is exoenergetic by 144.3 kcal/mol. Evaluating the Born hydration energy of AlO_2^- and $Al(OH)_4^-$ using the Rashin and Honig (1985) approach reduces the magnitude of the solution energy difference only very slightly, to 141.6 kcal/mol. It is not possible to obtain a supermolecule result for the species AlO_2^- since the first two water molecules added enter the nearest-neighbor sphere. Although the $AlO_2(H_2O)_2^-$ species formed is a local minimum on the energy surface it is about 120 kcal/mol higher in energy than $Al(OH)_4^-$. A similar problem arises for $Al(OH)_3$, which is calculated to add water with an energy decrease of 24.1 kcal/mol to form $Al(OH)_3H_2O$ (eq. 2 in Table 5). A supermolecule of composition $Al(OH)_3...6H_2O$ (i.e., three -OH molecules in the nearest-neighbor coordination sphere and six -OH$_2$ molecules in the first hydration sphere) also cannot be obtained—one of the water molecules enters the nearest-neighbor sphere to give a composition $Al(OH)_3H_2O...5H_2O$. Thus, we suggest that the chemical species AlO_2^- and $Al(OH)_3$ are not stable in aqueous solution and that they should not be used in the formulation of the reactions which actually occur.

For Equation 2 (modeled by reaction 3 in Table 5) we consider the formation of hexahydrated $Al(OH)_4^-$ plus aqueous H^+ from hexahydrated $Al(OH)_3H_2O$. We find this process to be unfavorable energetically by 2.3 kcal/mol at the Hartree-Fock level. There are however several important approximations included within this result. First, we evaluate the stabilization of $Al(OH)_4^-...6H_2O$ from all the further hydration shells using a Born model and we ignore any contribution to the stability of the neutral $Al(OH_3)H_2O...6H_2O$ from such further hydration shells. This approximation might favor the $Al(OH)_4^-...$ species. We tested this by performing SCRF calculations on the $Al(OH)_3H_2O...6H_2O$ and $Al(OH)_4^-...6H_2O$ supermolecules, finding that the polarization stabilization was indeed larger for the $Al(OH)_3H_2O$ species, but only by about 1.2 kcal/mol. In general, such polarization effects will be much smaller for a supermolecule than for the bare, unhydrated species. We have therefore ignored this small effect in the following analysis. Second, the results in Table 5 are for internal energies at the Hartree-Fock level. Table 6 gives details on correlation contri-

TABLE 5. Calculated energies for various reactions in solution, evaluated at the polarized SBK Hartree-Fock level

Reaction	ΔE_{HF} gas-phase	Born hydration energy	Total energy of reaction in solution	
	au	au	au	kcal/mol
(1) $AlO_2^- + 2\,H_2O \rightarrow Al(OH)_4^-$	−0.2299	+0.0043	−0.2256	−141.6
(2) $Al(OH)_3 + H_2O \rightarrow Al(OH)_3H_2O$	−0.0384		−0.0384	−24.1
(3) $Al(OH)_3H_2O...6H_2O \rightarrow Al(OH)_4^-...6H_2O + H^+$	+0.4767	−0.473	+0.0004	+2.3
(4) $Al(OH_2)_6^{3+} \rightarrow Al(OH_2)_5OH^{2+} + H^+$	0.0742	−0.037	+0.037	+23.2
(5) $Al(OH)_4^- + 4\,H_2O + 2\,H^+ \rightarrow Al(OH_2)_6^{3+} + 2\,OH^-$	+0.1145	−0.142	−0.027	−16.9
(6) $Na(H_2O)_6^+ + Al(OH)_4^-...6H_2O \rightarrow NaAl(OH)_4...11H_2O + H_2O$	−0.0864	0.114	+0.028	17.6
(7) $NaAl(OH)_4...10H_2O + H_2O \rightarrow NaAl(OH)_4...11H_2O$	−0.0450		−0.0450	−28.2

butions, zero-point energy, and temperature dependent enthalpy and entropy contributions, using computational results for the bare gas-phase species $Al(OH)_3H_2O$ and $Al(OH)_4^-$. Correlation effects are estimated using the MP2 method (at the MP2 equilibrium geometries). The entropy change is obtained from the calculated entropies of gas-phase $Al(OH)_3H_2O$ and $Al(OH)_4^-$, the experimental entropy of solution of H^+ (Marcus 1986) and a small correction (≈ 0.6 kcal/mol contribution to $-T\Delta S$) for the electrostatic Born hydration entropy of $Al(OH)_4^-...6H_2O$, obtained using the formula of Marcus (1986). After adding in all these terms we obtain a free energy change of +0.5 kcal/mol for this reaction, so that the equilibrium constant of reaction 2 will be close to 1. It is also useful to compare the hydrolysis of $Al(OH)_3H_2O$ with that of $Al(OH_2)_6^{3+}$, which is shown as Equation 4 in Table 5. Using the same approach as for $Al(OH)_3H_2O$ we find an energy change in solution of +25.8 kcal/mol for the $Al(OH_2)_6^{3+}$ hydrolysis. Thus, we calculate that the hydrolysis of $Al(OH)_3H_2O$ is much more favorable energetically than that of $Al(OH_2)_6^{3+}$, which is known experimentally to hydrolyze extensively unless the pH is quite low. This suggests that $Al(OH)_3H_2O$ will be hydrolyzed extensively to $Al(OH)_4^-$ not just at neutral pH but at low pH as well.

In Equation 5 of Table 5 we consider the relative stability of $Al(OH)_4^-$ and $Al(OH_2)_6^{3+}$, finding $Al(OH_2)_6^{3+}$ to be somewhat more stable at neutral pH, although of course it could hydrolyze to some "$Al(OH)^{2+}$" species. The energy difference calculated for Equation 5 would correspond to a log equilibrium constant value of about +9, but clearly from the stiochiometry of the reaction we can easily drive the formation of either ion by modifying the pH of the solution.

The energy components for formation of the fully hydrated solvent-separated $NaAl(OH)_4$ ion pair, $NaAl(OH)_4..11H_2O$, is given in Equation 6 of Table 5. The gas-phase energy change

for the ions with the first hydration sphere water molecules is favorable, but when the change in Born hydration energy is added the overall process becomes unfavorable energetically by about 18 kcal/mol. This value is fortuitously close to the 15.0 kcal/mol value determined experimentally for ΔH at 298 K by Diakonov et al. (1994). Of course, as for the $Al(OH)_3H_2O$-$Al(OH)_4^-$ case, there is a potential problem arising from inclusion of second and higher hydration sphere effects for the ions, based upon the Born model, and the truncation to the first hydration sphere of the contributions for the neutral ion pair. A SCRF calculation on $NaAl(OH)_4...11H_2O$ at the dipole level of the multipole expansion indeed gives a stabilization energy of about 22 kcal/mol. We have not included this since we feel that this truncation of the multipole expansion may give inconsistent results for $NaAl(OH)_4...11H_2O$ compared to the more symmetric $Na(H_2O)_6^+$ and $Al(OH)_4^-...6H_2O$ ions. Equation 7 involves the addition of a single water molecule to form the solvent-separated ion pair from the contact ion-pair. This process is favorable by about 28 kcal/mol, which is about the same energy as that for reaction of bare Na^+ with a single water (24.3 kcal/mol). Thus, it is clear that the solvent-separated ion pair is more favorable than the close-contact ion pair. It is of course the presence of H_2O at the center of $NaAl(OH)_4...11H_2O$, which renders most of its properties so much like those of the isolated ions.

DISCUSSION

$Al(OH)_3H_2O$ is a stable species in water, with a well defined nearest-neighbor coordination sphere, and with well defined distances, vibrational frequencies and NMR shieldings. Our calculations indicate that $Al(OH)_3H_2O$ can be distinguished from $Al(OH)_4^-$ by IR and Raman although its Al NMR shielding will be almost the same. In addition the ^{17}O and ^1H NMR spectra of $Al(OH)_3H_2O$ and $Al(OH)_4^-$ will be substantially different. $Al(OH)_3H_2O$ is calculated to have almost the same internal energy as $Al(OH)_4^-$ plus H^+. Based on the calculation of enthalpic and entropic contributions for the bare gas-phase species $Al(OH)_3H_2O$ and $Al(OH)_4^-$, and comparison with results for $Al(OH_2)_6^{3+}$, $Al(OH)_3H_2O$ should be extensively hydrolyzed to $Al(OH)_4^-$.

The stable Na-aluminate ion-pair species is calculated to be the fully hydrated solvent separated ion pair $NaAl(OH)_4...11H_2O$. Its calculated Al-O stretching frequencies are only slightly smaller than those for $Al(OH)_4^-...6H_2O$. The Al NMR properties of $Al(OH)_4^-...6H_2O$ and $NaAl(OH)_4...11H_2O$ are also very similar but the Na is calculated to be deshielded in the ion

TABLE 6. Additional energetic and entropic terms (in kcal/mol), evaluated for unhhydrated species at $T = 298$ K

Reaction	$Al(OH)_3H_2O \rightarrow Al(OH)_4^- + H^+$	$Na^+ + Al(OH)_4^- \rightarrow NaAl(OH)_4$
ΔE_{HF} (solution)[†]	+2.3	+17.6
$\Delta E_{MP2} - \Delta E_{HF}$	−4.2	−0.6
ΔE_{ZPE}	−8.8	−1.7
$-T\Delta S$ (solution*)	+11.8	−14.9
ΔH ($T = 298$) change	−0.6	+1.3
ΔG_{total}	+0.5	+1.7

* Experimental values used for ΔS_{hyd} of H^+ and Na^+ and electrostatic Born terms added for $Al(OH)_4^-...6H_2O$ using the formula of Marcus (1986).
† From Table 5.

pair by about 5 ppm. Calculated values for the enthalpy and entropy change for formation of the ion pair, reaction 3, are in reasonable agreement with the experimental results of Diakanov et al. (1994, 1996) and Pokrovskii and Helgeson (1995) and confirm a substantial stability for this ion pair.

It is important to note that the energetics calculated have been for T = 298 K. At higher temperatures and pressures in aqueous solutions neutral species like $Al(OH)_3H_2O$ and $NaAl(OH)_4$ would be favored both because of a decrease in the dielectric constant of the medium and because their formation leads to a significant increase in the entropy of the solution.

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