

Structure and stability of aluminum-silica complexes in neutral to basic solutions. Experimental study and molecular orbital calculations

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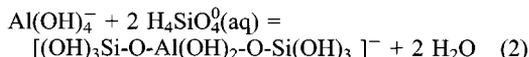
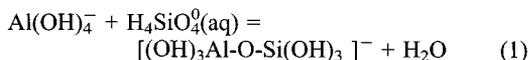
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The stability of $\text{AlH}_3\text{SiO}_4^{2+}$, the aqueous complex formed in acid solutions between Al^{3+} and $\text{H}_4\text{SiO}_4^0(\text{aq})$, has been recently quantified in the temperature range 25–300°C at P_{sat} (Pokrovski *et al.*, 1996; Salvi *et al.*, 1998). It was found that the stability of $\text{AlH}_3\text{SiO}_4^{2+}$ strongly increases with temperature and this complex can dominate Al speciation in strongly acidic high temperature fluids. To assess the possible effect of aluminum-silica aqueous complexing at the neutral to basic conditions typical of most crustal fluids an experimental study including potentiometric titrations, ^{27}Al NMR measurements, and boehmite solubility determinations was combined with molecular orbital calculations. The results reported in this study allow accurate determination of the thermodynamic properties of aluminum-silica complexes formed in neutral to basic solutions, thus providing new insights on Al transport and water-aluminosilicate interactions in natural systems.

Results and discussion

Potentiometric titrations of Al- and Si-bearing solutions ($10^{-4} < (\text{Al}, \text{Si}) < 10^{-3} \text{ m}$) were performed at 25 and 75°C, and $9 < \text{pH} < 13$ while ^{27}Al NMR spectra of similar Al- and Si-bearing solutions were obtained at 25°C and $\text{pH} > 8$. Boehmite solubility measurements were performed as a function of aqueous silica concentration at 200 and 300°C. Results are consistent with the formation of single Al-substituted Q^1_{Al} silica dimer and Q^2_{Al} silica trimer (see Fig. 1) according to:



respectively. However it was found that the concentration of the Q^2_{Al} trimer is negligible compared to that of the Q^1_{Al} dimer at aqueous silica concentrations typical of most natural fluids. Logarithm of equilibrium constants for reaction (1) ($\text{Log } K_1$) found in this study are: 3.77 ± 0.13 , 3.36 ± 0.20 , 2.67 ± 0.20 , and 2.32 ± 0.20 at 25, 75, 200, and 300°C, respectively. $\text{Log } K_1$ is linearly related to the reciprocal temperature, yielding a heat capacity and enthalpy of reaction (1) of 0 and -17.6 kJ/mol, respectively.

Molecular orbital calculations were carried out with GAUSSIAN 94. Minimum potential structures for the molecules $\text{Al}^{3+} \cdot 6(\text{H}_2\text{O})$, $[\text{Al}(\text{OH})_4]^- \cdot 2(\text{H}_2\text{O})$, $[(\text{OH})_3\text{Al}-\text{O}-\text{Si}(\text{OH})_3]^-$, $[(\text{OH})_3\text{Si}-\text{O}-\text{Al}(\text{OH})_2-\text{O}-\text{Si}(\text{OH})_3]^-$ were calculated using self-consistent, Hartree-Fock molecular orbital calculations with 3-21G** basis sets to determine minimum energy structures. Al chemical shift calculations were performed using these structures and HF/6-31G*

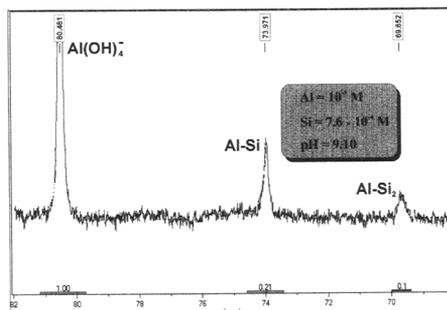


FIG. 1. ^{27}Al NMR spectrum of an aluminosilicate solution at 25°C.

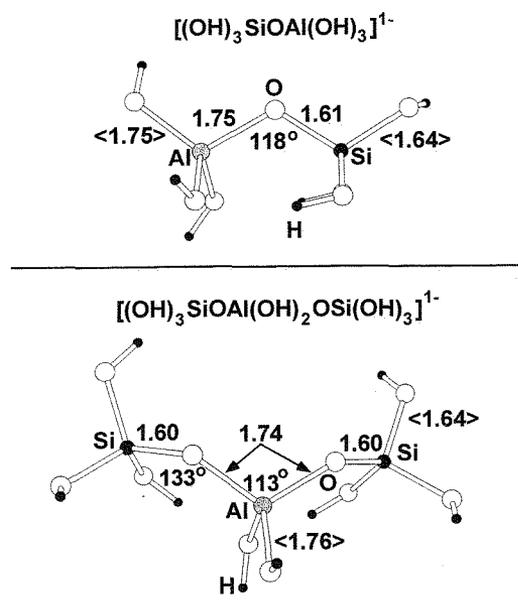


FIG. 2. Optimized geometries (HF/6-31G*) of aluminum silica aqueous complexes. Distances in Å, "< >" indicates an average of T-(OH) bonds.

basis sets and the gauge-including atomic orbital method (see calculational details in Sykes *et al.*, 1997). The optimized geometries for the above aqueous aluminosilicate complexes are shown in Fig. 2. Model prediction of ^{27}Al NMR spectra on aqueous Al and aluminosilicate complexes are compared with experimental values in the Table. It can be seen that the HF/6-31G* calculation predicts relative ^{27}Al chemical shifts very close to the experimental values thus confirming experimental shift assignments. Note that the higher level HF/6-311+G(3df,2p) calculations overestimate the chemical shifts. Hence, compensating errors may give fortuitously accurate values for the presumably less accurate HF/6-31G* calculations. Self-consistent isodensity polarized continuum model (SCIPCM) calculations with a HF/6-311+G** basis set predict $\Delta E = -10$ kJ/mol for reaction (1) at 25°C which is in

TABLE 1. ^{27}Al NMR Chemical shifts (in ppm)

	HF/6-31G*	HF/6-311+G(3df,2p)	Experimental value
Al^{3+}	0	0	0
$\text{Al}(\text{OH})_4^-$	78	86	80.5
Q_{Al}^1	74	81	74
Q_{Al}^2	68	—	69.5

good agreement with the experimentally derived enthalpy of this reaction.

Calculations performed using the standard thermodynamic properties and HKF equation of state parameters generated in this study show that $[(\text{OH})_3\text{Al-O-Si}(\text{OH})_3]^-$ accounts for 80% of total dissolved aluminum in the presence of 30 ppm aqueous silica at temperatures less than 90°C. It can represent more than 95% of total aluminum in Icelandic and Pyrenean natural waters and thus enhance aluminosilicates weathering rates. At higher temperatures, the decrease in $\text{Log } K_1$ is matched by an increase of aqueous silica concentration in most natural systems. For example, Al-Si complex formation increases Al concentration by an order of magnitude in solutions in equilibrium with the kaolinite-quartz assemblage at 300°C and $\text{pH} > 4$. It follows that accurate calculation of mineral dissolution rates, solubility, and mass transport during water-aluminosilicate interaction requires explicit provision for Al-Si complexing, at both surficial and hydrothermal conditions.

References

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