# Experimental study of Na-Al complexing in hydrothermal solutions

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## Introduction

Although the solubility of aluminium oxides, hydroxides and silicates are extremely low in aqueous solutions at the pHs and temperatures encountered in most sedimentary and hydrothermal environments, there is much evidence that aluminium transport occurs in these systems. For a significant aluminium transport to develop, it is necessary for aluminium to form complexes with organic and inorganic ligands. Several recent studies have demonstrated that organic anions are likely to enhance aluminium solubility (Benezeth et al., 1994, Palmer and Bell, 1994). For example, Benezeth et al. (1994) showed that at 170°C and weakly acidic conditions, the addition of 10,000 ppm acetate will increase the concentration of aluminium in equilibrium with the mineral assemblage albite-quartz-kaolinite by nearly one order of magnitude. There has been also recent speculation that K and Na form complexes with $Al(OH)_4^-$ at high pressures and temperatures (Pokrovskii and Helgeson, 1992). However, no experimental investigations have been performed to date to establish the stability of such complexes over a wide range of temperatures and pressures. The purpose of this study is to present values of the stability constant of $NaAl(OH)_4^0$ generated from solubility and potentiometric measurements up to 325°C, and to evaluate the role of this complex in geochemical processes at elevated temperatures.

## Experimental procedures

*Solubility measurements.* Boehmite solubility was measured at saturated vapor pressure between 90 and 325°C. Synthetic boehmite was obtained via a hydrothermal treatment (300°C, deionized water) of pure synthetic gibbsite. Solubility experiments at 90°C were performed in polypropylene containers immersed in a water thermostated bath. At higher temperatures, experiments were performed in titanium reactors which allowed in situ sampling of solutions. Solutions were stirred by rocking the autoclaves and maintained at constant temperature ($\pm$ 2°C). Experiments were carried out in $NH_4OH/NH_4Cl/NaCl$ and $NaOH/NaCl$ solutions prepared from Prolabo Reagent Grade chemicals. NaCl concentrations varied from 0.1 to 1 mol/l. During each run solution was sampled regularly to measure the pH and Al concentration. pH was measured using Schott combined electrode using three NBS standard solutions (4.01, 6.87, 9.18). Al content was measured by flame and flameless atomic absorption, using standards with solution matrixes that matched those of the samples. The activity of $NaAl(OH)_4^0$ complex was calculated resolving a system of equilibrium, mass and charge balance equations, using a Newton-Raphson method, boehmite dissociation constants from Castet et al.(1993), dissociation constants for $H_2O$, $NH_4Cl$, NaOH, NaCl compiled by Castet et al.(1993), and dissociation constants of $NH_4OH$ from Hitch and Mesmer (1976 ). Activity coefficients were calculated using equations reported by Helgeson et al. (1981).

*Potentiometric measurements.* Potentiometric measurements were performed with new sodium selective glass electrodes developed by the company 'POTENTIAL' (Beliustin et al., 1992) and which can operate up to 200°C. The following cell with a liquid junction was used: Sn-Cu, Li-Sn alloy // glass // test solution with Na / 3.2MKCl, Ag/AgCl. The measurements were carried out in 0.18M NaCl–0.07M NaOH and 0.18M $NaAl(OH)_4$–0.07M NaOH solutions. The detailed description of the potentiometric apparatus, electrodes characteristics, and the calculation procedures are given elsewhere (Pokrovski et al., 1994).

## Results

The logarithms of the association constant of $NaAl(OH)_4^0$ determined in this study are plotted in Fig.1 as a function of temperature. It can be seen

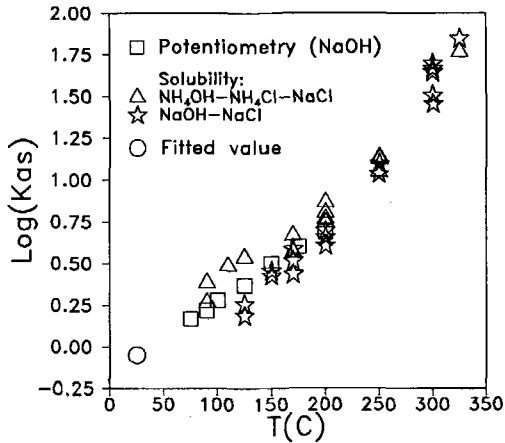FIG. 1. Logarithm of the association constant of NaAl(OH)$_4^0$ as a function of temperature.
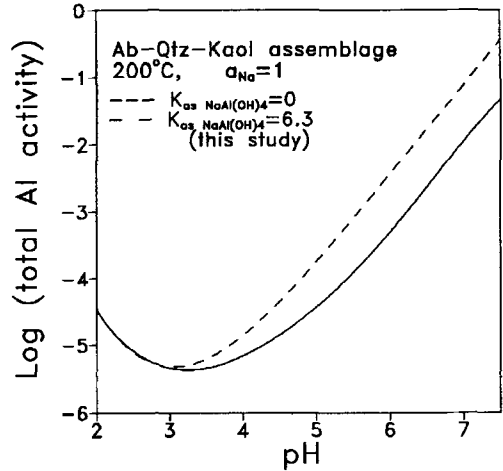


FIG. 2. Calculated total aluminium activity as a function of pH in an aqueous solution at equilibrium with the mineral assemblage albite-quartz-kaolinite.

that the values deduced from solubility and potentiometric measurements are in close agreement ($\Delta \log K \leqslant 0.2$). The stability constant of NaAl(OH)$_4^0$ increases markedly with temperature and reaches a value of $\sim$ 100 at 325°C. Fitting our experimental data to an equation of the type:

$$LnK_{as} = A + B/T + C \cdot lnT + D \cdot T$$

yields the following thermodynamic properties for NaAl(OH)$_4^0$ at 298K: LogK as $= -0.05 \pm 0.2$, $\Delta_f G° = -1567.6$ kJ/mol, S° $= 216.2$ J/mol.K, C$_p^0$ $= 64.1$ J/mol.K. The association constants generated in this study are in good agreement with those predicted by Pokrovskii and Helgeson (1994) above 150°C. However, strong Al-Na association was found at low temperatures in contrast to the results of Pokrovskii and Helgeson (1992), who reported a value of logK$_{as} = -0.75$ at 25°C. Note the stability constants measured for NaAl(OH)$_4^0$ are very close to those found for NaB(OH)$_4^0$ via potentiometric measurements by Pokrovski et al. (1994). From the data generated in this study it is expected that Na-Al complexing is likely to control aluminium transport in sodium-rich crustal fluids. For example, the computed aluminium activity in equilibrium with the mineral assemblage albite-quartz-kaolinite at 200°C in 1M NaCl solution is depicted in Fig.2. The equilibrium constant for the reaction $3Al^{3+}$ + albite + quartz + $8H_2O$ = 2kaolinite + Na$^+$ + 8H$^+$ was calculated from the data reported by Bowers et al. (1984). It can be seen in Fig. 2 that Na-Al complexing increases the equilibrium concentration of aluminium by an order of magnitude. Note also that NaAl(OH)$_4^0$ forms at pHs commonly met

in hydrothermal solutions.

Thus, it can be concluded that Al-Na complexing should not beignored in most of crustal fluids.

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