Experimental study of aluminum–fluoride complexation in near-neutral and alkaline solutions to 300 °C

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Abstract

Solubility of boehmite (from 90 to 300 °C) and gibbsite (at 44.5 °C) was measured as a function of NaF concentration in alkaline NH_4OH-NH_4Cl-(NaCl) solutions at saturated vapor pressure. The marked increase of boehmite and gibbsite solubility in the presence of fluorine is explained by the formation of $Al(OH)_2F_2^-$ according to $Al(OH)_4^- + 2F^- = Al(OH)_2F_2^- + 2OH^-$. Log K values regressed from these data at 44.5, 90, 150, 200, and 300 °C are -6.51 ± 0.15, -5.06 ± 0.10, -3.98 ± 0.10, -3.49 ± 0.15, and -2.86 ± 0.20, respectively. The dependence of log K on temperature is precisely described (within ± 0.07 log unit) by the function $pK = -\log K = 7297.15/T(K) - 81.53 + 11.29 \cdot \ln T(K)$ whose differentiation with respect to T yields the following thermodynamic properties for this reaction: log $K_{298.15} = -7.26$, $\Delta_r H°_{298.15} = 75.28$ kJ/mol, and $\Delta_r S°_{298.15} = 113.4$ J/mol K. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Numerous observations indicate that the presence of fluorine can markedly enhance Al transport in natural surface waters and in crustal fluids. Aluminum–fluoride complexes dominate aqueous Al speciation in forest soils (Mitrovic and Milacic, 2000) and in fluorine-rich hot springs discharging in granite areas (Michard et al., 1979). Moine et al. (1998) and Zaraisky (1994) have reported important Al migration linked to fluorine during the formation of skarn and greisen ore deposit. Besides, the presence of fluorine in aqueous solutions yields an increase of dissolution rates of aluminum oxides and oxyhydroxides (Kraemer et al., 1998; Nordin et al., 1998). Knowledge of the identity and stability of aqueous complexes formed between aluminum and fluorine is thus essential for modeling Al transport in natural fluids.

The stability of aluminum–fluoride species, $Al F_n^{3-n}$, and mixed hydroxide fluoride complexes, $Al(OH)_m F_n^{3-m-n}$, formed in acid solutions has been determined to 50 °C by Baumann (1969) and Couturier (1986), and at 300–600 °C by Zaraisky (1994). In near-neutral and alkaline solutions, which account for most crustal fluids, aluminum–fluoride complexation was only investigated to 50 °C by Couturier (1986) who found that $Al(OH)_3F^-$ was the dominant Al species. However, the last data were obtained in too narrow

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temperature, pH and pF intervals to allow extraction of reliable thermodynamic information.

The present study is aimed at filling this gap and providing accurate data on the complexation of aluminum with fluoride at near-neutral and alkaline conditions where $Al(OH)_4^-$ is the dominant Al hydroxide species. For this purpose, gibbsite and boehmite solubility have been measured as a function of temperature in pH-buffered alkaline solutions with and without fluoride.

2. Materials and methods

2.1. Preparation of solids and experimental solutions

The method of boehmite (γ-AlOOH) preparation is described in several publications (e.g., Castet et al., 1993; Diakonov et al., 1996). Briefly, it consisted in reacting synthetic gibbsite (α-Al(OH)$_{3(s)}$, Riedel, De Haen AG SEELZE, Hannover 2504361) with deionized water at 300 °C and P_{sat} for 2 weeks. The solution was separated from the solid via filtration through a 10-μm Ti filter at 300 °C to avoid precipitation of other Al hydroxides. The powder was subsequently repeatedly rinsed at 25 °C with deionized water and allowed to react with deionized water an additional week at 300 °C. Then the solution was again separated from the solid as described above. XRD and gravimetric analysis showed the obtained phase to be pure well-crystallized boehmite with a slight excess of water (about 1%) compared to the theoretical concentration.

Synthetic gibbsite (the same as for boehmite synthesis) was used for solubility measurements at 44.5 °C. No special preparation of this phase was made.

Experimental solutions were prepared from degassed doubly deionized water provided by a Milli-Qplus® system, Pro Analysi® Merck NaCl, NaF and NH$_4$Cl salts, and Suprapur® NH$_4$OH (about 28 wt.% NH$_3$). The starting solutions were prepared immediately prior to each experiment. Doubly distilled HNO$_3$ was used to acidify sampled solutions and prepare standard solutions for Al analyses.

2.2. Solubility measurements

Gibbsite and boehmite solubility was measured at P_{sat} as a function of concentration of NaF in NH$_4$OH-

NH$_4$Cl-(NaCl) solutions at 44.5 and from 90 to 300 °C, respectively. Experiments were performed in stainless steel Prolabo autoclaves (at 200 and 300 °C), but in pure titanium autoclaves at 150 °C and for a few experiments at 200 °C. About 200–250 ml of experimental solution together with 0.25 g of boehmite were used in each experiment. Air was replaced by pressurized nitrogen. The autoclaves were placed in rocking furnaces, which allow mixing of experimental solutions and thus minimization of temperature gradients. Temperature in the autoclaves was maintained constant (± 1 °C) and measured with externally calibrated thermocouples. Solution sampling started a few days after attainment of thermal equilibrium and then proceeded at least 1 week. A 10-μm Ti filter installed inside the autoclave permitted in situ filtration. Then, the solution was passed through a 0.1–0.45-μm Sartorius filter directly into 0.5 M HNO$_3$ to obtain a $\sim$0.1 M HNO$_3$ sample solution. To test the formation of other solid phases than boehmite during autoclave heating, an experiment was performed at 200 °C with injection of boehmite only when equilibrium temperature was reached. No difference was observe between this experiment and those for which boehmite was introduced before heating. This proves that boehmite controlled Al concentration in autoclave experiments. No change of the solid phase during experiments up to 0.01m NaF was detected using XRD.

Experiments at 90 and 44.5 °C were performed in titanium reactors and polypropylene flasks, respectively. About 200 ml of an experimental solution was placed into each reactor (flask) together with 0.1–0.2 g of the solid phase (boehmite at 90 °C and gibbsite at 44.5 °C). Air was removed with nitrogen, reactors (flasks) were hermetically closed and immersed in thermometrically controlled water bath (within ± 0.5 °C). A hole in the cover allowed sampling of the solution by means of a 20-ml polyethylene syringe. The samples were immediately filtered at run temperature into HNO$_3$ using a titanium filtration cell with a 0.45-μm Sartorius filter.

2.3. Analytical methods

For experiments at 45.5 and 90 °C, pH was in situ measured using an Orion Ross 8104 combination glass electrode standardized on an activity scale using DIN 19266/NBS standards (pH = 6.865 and 9.180 at

25 °C). Accuracy of measurements was ± 0.01 pH unit.

Final (after experiments) concentration of fluorine was determined either with a Tacussel fluoride selective electrode in solutions containing less than $0.1m$ NH_3 or, at higher concentration, via ion chromatography (Dionex 4000I chromatograph). Initial (before experiments) solutions were used as standards to minimize matrix effect. Before potentiometric measurements, TISAB III pH and ionic strength adjuster was added to samples and standards. Accuracy of fluoride analysis was 5% for both methods.

Al concentration was determined by flameless atomic absorption spectroscopy in a graphite furnace with a Perkin Elmer 5100 PC spectrophotometer with an accuracy of 5% at a 95% confidence level. The method of analysis is described in detail by Salvi et al. (1998). Concentration of Al in several samples was checked by ICP-MS. The difference between these two methods was 1% of total Al concentration.

2.4. Calculation of chemical equilibria and stability constants

Standard state adopted in the present study for the aqueous species was unit activity for a hypothetical, one molal ideal solution. For a pure mineral and H_2O, the standard state corresponds to a unit activity of the pure phase at given temperature and pressure. The activity coefficients of charged aqueous species were calculated according to Helgeson (1969),

$$\log \gamma_i = \frac{Az_i^2 \sqrt{I}}{1 + Ba\sqrt{I}} + \Gamma_\gamma + B\bullet(T)\cdot I \tag{1}$$

Γ_γ designate the mole fraction to molality conversion factor ($\Gamma_\gamma = -\log\ (1 + 0.0180153\ m*))$ and $m*$ corresponds to the sum of the concentrations of all solute species. $B\bullet$ corresponds to the deviation function at any given temperature; z_i denotes to charge of ith species; a, the ion size parameter, is taken equal to 4.5 Å for all species. For neutral species it was assumed:

$$\log \gamma_n = \Gamma_\gamma. \tag{2}$$

The thermodynamic properties of aqueous species except those of Al were calculated using SUPCRT92 code and data base (Johnson et al., 1992). In this computer code $S°_{298.15}$ and $\Delta_f H°_{298.15}$ for NH_4^+ were accepted from CODATA (1978), $\Delta_f G°_{298.15}$ was computed from these values and the standard partial molal entropies from CODATA (1978). The partial molal volume and heat capacity of NH_4^+ reported in SUPCRT92 were calculated in Tanger and Helgeson (1988). The thermodynamic properties of $NH_3^0{}_{(aq)}$ are reported in Shock et al. (1989) where the values of $\Delta_f G°_{298.15}$, $S°_{298.15}$ and $\Delta_f H°_{298.15}$ were accepted from Vanderzee et al. (1972), and $C_p°$ and $V°$ taken from Allred and Woolley (1981). NaOH and NH_4Cl dissociation constants were taken from Shock et al. (1997) and Castet et al. (1993), respectively. Values of the

Table 1

Values of the logarithms of the dissociation constants of H_2O, HF, HF_2^-, NaF, NH_4^+ NH_4Cl, NaCl, and NaOH (at saturated water vapor pressure) used in this study

T (°C)	$\log K(H_2O)$[a]	$\log K(HF)$[b]	$\log K(HF_2^-)$[c]	$\log K(NaF)$[d]	$\log K(NH_4^+)$[e]	$\log K(NH_4Cl)$[f]	$\log K(NaCl)$[g]	$\log K(NaOH)$[h]
44.5	-13.42	-3.36	-2.78	0.91	-8.68	0.71	0.71	0.20
90	-12.42	-3.75	-3.28	0.68	-7.61	0.52	0.52	0.14
150	-11.63	-4.34	-3.88	0.34	-6.52	0.21	0.21	0.01
200	-11.28	-4.86	-4.37	0.01	-5.80	-0.09	-0.09	-0.15
300	-11.30	-6.14	-5.58	-0.95	-4.68	-1.01	-1.01	-0.82

[a] $H_2O = H^+ + OH^-$, SUPCRT92, Johnson et al. (1992).
[b] $HF^0{}_{(aq)} = H^+ + F^-$ SUPCRT92, Johnson et al. (1992).
[c] $HF_2^-{}_{(aq)} = H^+ + 2F^-$, SUPCRT92, Johnson et al. (1992).
[d] $NaF^0{}_{(aq)} = Na^+ + F^-$, SUPCRT92, Johnson et al. (1992).
[e] $NH_4^+ = NH_3^0{}_{(aq)} + H^+$, SUPCRT92, Johnson et al. (1992).
[f] $NH_4Cl^0{}_{(aq)} = NH_4^+ + Cl^-$, Castet et al. (1993).
[g] $NaCl^0{}_{(aq)} = Na^+ + Cl^-$, SUPCRT92, Johnson et al. (1992).
[h] $NaOH = Na^+ + OH^-$, Shock et al. (1997).

Table 2
Composition of experimental solutions, solubility [Al total, (mol/kg H$_2$O)] of gibbsite (at 44.5 °C) and boehmite (at 90, 150, 200, and 300 °C), and measured or calculated pH at saturated water vapor pressure

m(NH$_4$OH)	m(NH$_4$Cl)	m(NaCl)	m(NaF) $\times 10^3$	m(Al) $\times 10^6$	pH[a]
44.5 °C					
0.010	0.10	0.050	0.0	1.21	7.86
0.010	0.10	0.048	2.0	1.21	7.84
0.010	0.10	0.046	4.0	1.62	7.83
0.010	0.10	0.046	4.0	1.38	7.86
0.010	0.10	0.044	6.0	2.34	7.84
0.010	0.10	0.044	6.0	2.25	7.85
90 °C					
0.020	0.06	0.050	0.0	1.69	7.26
0.020	0.06	0.050	0.0	1.61	7.23
0.020	0.06	0.050	0.0	1.54	7.23
0.020	0.06	0.050	0.5	1.62	7.25
0.020	0.06	0.049	1.0	2.08	7.25
0.020	0.06	0.049	1.0	1.79	7.25
0.020	0.06	0.048	2.0	2.39	7.25
0.020	0.06	0.0465	3.5	3.83	7.25
0.020	0.06	0.0450	5.0	7.01	7.26
0.020	0.06	0.042	8.0	10.0	7.27
0.020	0.06	0.042	8.0	11.8	7.26
150 °C					
0.050	0.050	0.050	0.0	8.74	6.69
0.050	0.050	0.048	2.0	26.3	6.69
0.050	0.050	0.050	5.0	77.6	6.69
0.050	0.050	0.040	10.0	341	6.69
0.050	0.050	0.030	20.0	974	6.69
200 °C					
0.30	0.010	0.010	0.0	161	7.36
0.30	0.010	0.010	0.0	166	7.36
0.30	0.010	0.0050	5.0	352	7.36
0.050	0.050	0.050	0	9.86	5.96
0.050	0.050	0.050	0.50	24.1	5.96
0.050	0.050	0.050	1.0	55.5	5.97
0.050	0.050	0.048	2.0	140	5.97
0.050	0.050	0.050	5.0	709	5.98
0.050	0.050	0.040	10.0	1250	5.98
300 °C					
0.30	0.020	0.0	0.0	32.8	6.02
0.30	0.020	0.0	0.0	35.9	6.02
0.30	0.020	0.0	0.50	85.3	6.03
0.30	0.020	0.0	1.0	157	6.03
0.30	0.020	0.0	2.0	419	6.05
0.30	0.020	0.0	2.0	276	6.05
0.30	0.020	0.0	5.0	1120	6.09
0.30	0.020	0.0	7.0	2020	6.11
0.050	0.020	0.050	0.0	14.4	5.36
0.050	0.020	0.048	2.0	336	5.40

Table 2 (continued)

m(NH$_4$OH)	m(NH$_4$Cl)	m(NaCl)	m(NaF) $\times 10^3$	m(Al) $\times 10^6$	pH[a]
300 °C					
0.306	0.0306	1.02	0.0	238	6.31
0.306	0.0306	1.02	0.0	260	6.31
0.307	0.0306	1.02	1.0	238	6.31
0.304	0.0306	1.02	2.04	602	6.31
0.304	0.0307	1.02	5.1	735	6.36

[a] pH measured at 44.5 and 90 °C, calculated for other temperatures.

dissociation constants used in the present study are listed in Table 1.

The stability constants of hydroxide fluoride complexes were calculated using FITEQL 3.1 computer code (Herbelin and Westall, 1994) at 90, 150, 200 and 300 °C by fitting all the data at the given temperature using activity coefficients calculated according to Eqs. (1) and (2). At 44.5 °C, the selected stability constants were calculated with the help of GIBBS computer code (Shvarov and Bastrakov, 1999).

3. Results and discussion

Solubility of boehmite (at 90, 150, 200 and 300 °C) and gibbsite (at 44.5 °C) together with measured (at 44.5 and 90 °C) and calculated (at $T > 100$ °C) pH values are listed in Table 2. No significant variation of Al concentration was observed in these runs after 1–3 days at 150–300 °C, 3 days at 90 °C, and 5 days at 44.5 °C. Calculated and measured pH at temperatures below 100 °C are within ±0.04 unit. Several attempts were made to measure boehmite solubility in > 0.02m NaF solutions but systematic decrease of F and Al concentrations with time was observed. This probably reflects formation of a new F-bearing solid phase. Only results of experiments for which no appreciable change of Al and F concentration occur with time are presented in Table 2.

Boehmite solubility measured in this study in fluoride-free solutions at all temperature is in good agreement with the data of Castet (1991), Castet et al. (1993), Diakonov et al. (1996) and Salvi et al. (1998). In contrast, gibbsite solubility was found to be 2.5 times higher than that measured by Wesolowski (1992) for an acid-treated Alcoa gibbsite. This solubility increase is connected either to the presence of

fine particles or amorphous aluminum hydroxide in the sample used in this study. However, it should not affect calculation of Al speciation as (i) the same solid phase was used for blank (without fluoride) and test (in the presence of NaF) experiments, and (ii) the absence of change of Al concentration with time

suggested that equilibrium was achieved in our experiments.

The log of boehmite solubility is plotted in Fig. 1a–d as a function of NaF concentration at constant pH and ionic strength. It can be seen that there is strong increase of solubility with fluorine concentration. Al
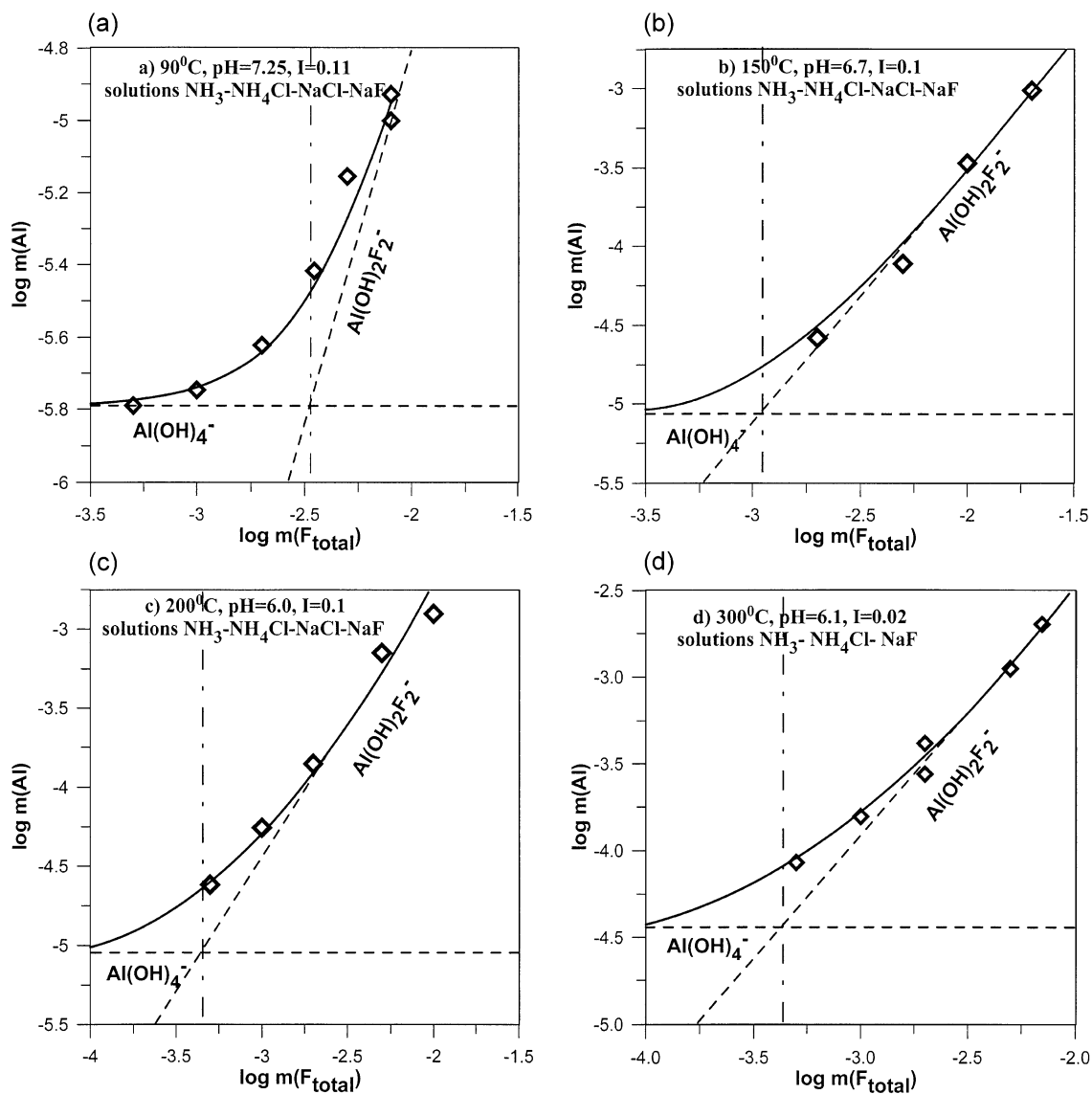
Fig. 1. Solubility of boehmite [total Al concentration in (mol/kg H$_2$O)] at constant pH and ionic strength as a function of aqueous NaF concentration at 90 (a), 150 (b), 200 (c), and 300 °C (d). Symbols represent experimental data, but the curves were calculated using values of the logarithm constant for reaction (4) listed in Table 3. The solid curve corresponds to the total concentration of aluminum, but dashed lines show concentration of Al(OH)$_4^-$ and Al(OH)$_2$F$_2^-$ species. Vertical dashed-dotted line separates domains of predominance of these species.

speciation calculations using different sets of thermo-dynamic data for Al hydroxide complexes (Shock et al., 1997; Tagirov and Schott, in press) shows that $Al(OH)_4^-$ accounts for more than 95% of total dissolved Al in all experiments performed in the absence of fluorine. As for each experimental run, T, pH, ionic strength and, therefore, $Al(OH)_4^-$ concentration were approximately constant, increase of Al concentration with fluoride concentration can be attributed to the formation of $Al(OH)_{4-n}F_n^-$ complexes according to:

$$Al(OH)_4^- + nF^- = Al(OH)_{4-n}F_n^- + nOH^- \qquad (3)$$
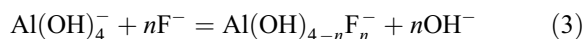
To check for the formation of different Al–F complexes, experimental data were fit using FITEQL computer code and assuming the formation of $Al(OH)_3F^-$, $Al(OH)_2F_2^-$ and both $Al(OH)_3F^- + Al(OH)_2F_2^-$. The $\log K$ values for the reactions,

$$Al(OH)_4^- + 2F^- = Al(OH)_2F_2^- + 2OH^- \qquad (4)$$

and

$$Al(OH)_4^- + F^- = Al(OH)_3F^- + OH^-, \qquad (5)$$
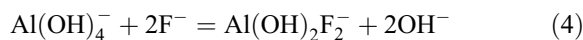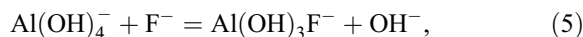
calculated using experimental data from this study are listed in Table 3. Note that thermodynamic and apparent (calculated using aqueous concentration) constant should be approximately equal as reaction (5) is isocoulombic (ionic charges of the same sign and magnitude appear on both sides of the equation ($\Delta z^2 = 0$)).

Deviation plots of measured Al concentrations, minus the values computed using stability constant given in Table 3, are shown as a function of temperature and total fluorine concentration in Figs. 2, 3 and 4. Figs.

a)

b)
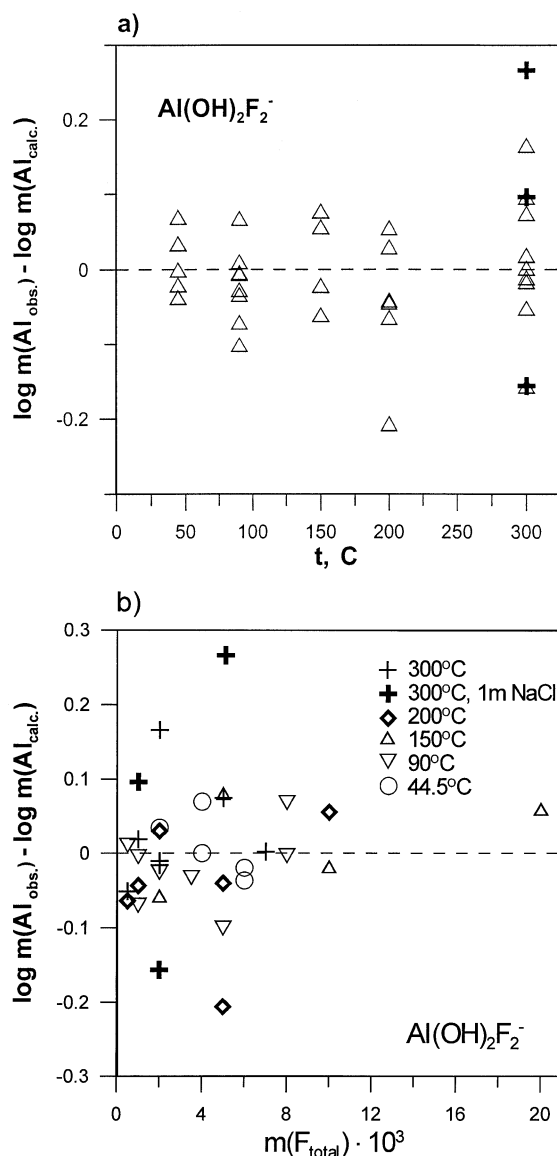
Fig. 2. Deviation plot of the measured $\log m(Al)$ minus the values computed from the formation constants of $Al(OH)_2F_2^-$ (first column in Table 3), as function of temperature (a) and total fluorine concentration (b).

2a and 3a demonstrate that for the speciation models that account for the formation of $Al(OH)_2F_2^-$ (Fig. 2a) and both $Al(OH)_3F^- + Al(OH)_2F_2^-$ (Fig. 3a), the scatter about the fit is within ± 0.2 log unit. The only point which comes out of these limits corresponds to high ionic strength ($1m$ NaCl at 300 °C, Fig. 2a) within the
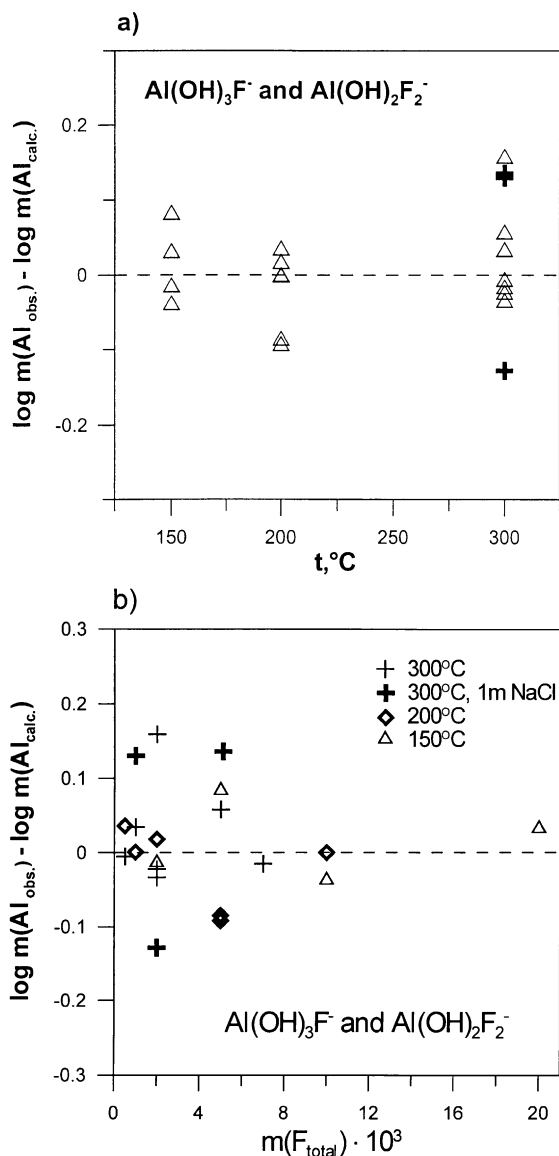
Table 3
Values of equilibrium constants for reactions (4) and (5) calculated using experimental data listed in Table 2

T (°C)	$\log K_{(4)}$[a]	$\log K_{(5)}$[a]	$\log K_{(4)}$[b]	$\log K_{(5)}$[b]
	I	II	III	IV
44.5	-6.51 ± 0.15	-3.46 ± 0.20		
90	-5.06 ± 0.10	-2.40 ± 0.10	–	-2.40 ± 0.10
150	-3.98 ± 0.10	-1.38 ± 0.20	-4.03 ± 0.10	-2.40 ± 0.25
200	-3.49 ± 0.15	-1.18 ± 0.20	-3.64 ± 0.10	-1.79 ± 0.10
300	-2.86 ± 0.20	-0.97 ± 0.20	-3.00 ± 0.10	-1.72 ± 0.10

[a] Calculated assuming presence of only one Al–OH–F complex.
[b] Calculated assuming presence of both $Al(OH)_3F^-$ and $Al(OH)_2F_2^-$ species.

a)

$Al(OH)_3F^-$ alone leads to much larger deviations (to 0.4 log unit, Fig. 4a). Besides, with this species, computed Al molalities at high fluorine concentrations are systematically lower than the observed values (Fig. 4b), which suggests presence of the complex contain-
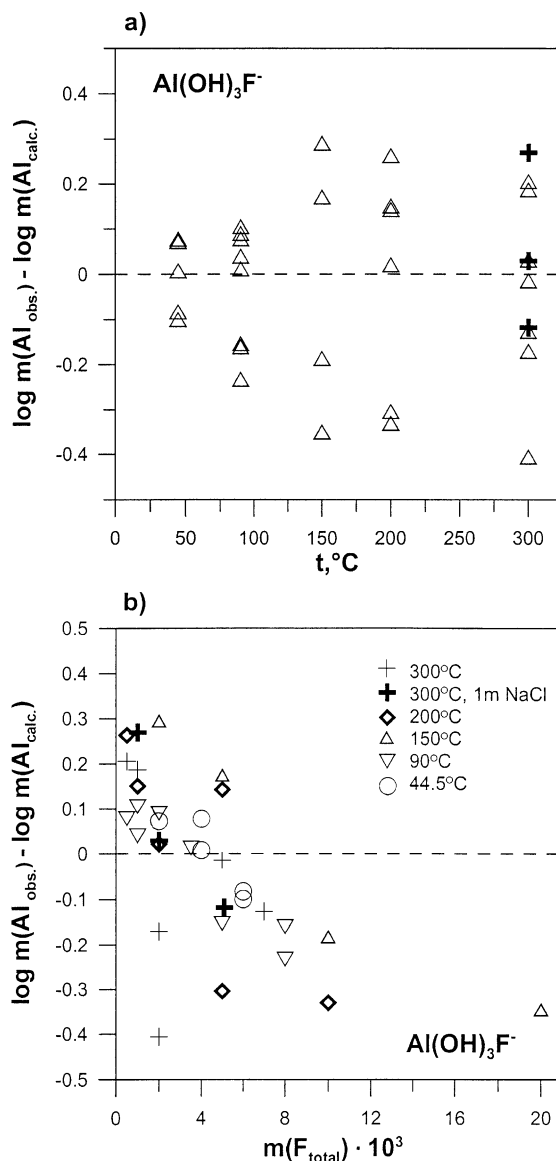
b)

Fig. 3. Deviation plot of the measured log $m(Al)$ minus the values computed from the formation constants of $Al(OH)_3F^- + Al(OH)_2F_2^-$ (third and fourth columns in Table 3), as a function of temperature (a) and total fluorine concentration (b).

a)

b)

Fig. 4. Deviation plot of the measured log $m(Al)$ minus the values computed from the formation constants of $Al(OH)_3F^-$ (second column in Table 3), as a function of temperature (a) and total fluorine concentration (b).

framework of the one-complex ($Al(OH)_2F_2^-$) speciation model. Examination of Figs. 2b and 3b shows that there is no systematic deviation of measured from computed Al concentration for $Al(OH)_2F_2^-$, and $Al(OH)_3F^- + Al(OH)_2F_2^-$ models. In contrast, use of

ing more fluorine. Therefore, the model based on $Al(OH)_3F^-$ was rejected.

The stability constants listed in Table 3 shows that calculated value of the equilibrium constant of reaction (4) changed only by 0.05 log unit at 150 °C and 0.14 log unit at 200 and 300 °C when $Al(OH)_3F^-$ was added to $Al(OH)_2F_2^-$. These small changes in log K are within the limits of the calculated overall uncertainty on log K values (Table 3), and deviation of observed minus calculated Al concentration (Figs. 2a and 3a). Thus, $Al(OH)_3F^-$ is unimportant at the experimental conditions of this study. Besides, examination of Eq. (3) shows that the number n of fluorine atoms in the dominant Al–F complex formed in our experiments is equal to the slope $S = $ dlog $m(Al)$/dlog $[F^-]$ or, as the fluoride-ion dominated fluorine speciation, $S \sim$ dlog $m(Al)$/dlog $m(NaF)$. It can be seen in Fig. 1b–d that the value of n at 150, 200, and 300 °C is close to 2. This confirms that $Al(OH)_2F_2^-$ is the dominant Al–F complex formed at these conditions.

At 90 and 44.5 °C, the increase in solubility is too small to make possible reliable calculation of the complex stoichiometry. Therefore, the same complex was assumed to be responsible for the increase of solubility at temperatures below 100 °C.

Difficulties connected with determination of $Al(OH)_3F^-$ stability are due to the stoichiometry of the exchange reaction:

$$Al(OH)_3F^- + F^- = Al(OH)_2F_2^- + OH^-, \qquad (6)$$

which shows that $Al(OH)_3F^-$ dominates at high pH and pF values. However, increase in pH give rise to increase of Al concentration due to formation of $Al(OH)_4^-$. This, in turn, demands higher fluorine concentrations to see the effect of F on Al speciation, and leads to the formation of $Al(OH)_2F_2^-$.

Several experiments were performed at 300 °C in $1m$ NaCl solutions (Table 2). Significant interaction between Na^+ and $Al(OH)_4^-$ with formation of $NaAl(OH)_4^0{}_{(aq)}$ has been predicted to occur at these conditions (Diakonov et al., 1996). The log $K = 1.11 \pm 0.20$, calculated in the present study for the reaction $Na^+ + Al(OH)_4^- = NaAl(OH)_4^0{}_{(aq)}$, is somewhat lower than the value given in Diakonov et al. (1996) (the log $K = 1.58$).

Couturier (1986) reported the equilibrium constant for the reaction (5) at temperatures 25, 37.5, and 50 °C.

To check the consistency of Couturier's (1986) data and those of this study, K_5 values listed in Table 3 (column II) were extrapolated to 25 °C using the equation $pK = A/T(K) - B + C \cdot \ln T(K)$. The calculated values of log $K_5 = -4.17, -3.71$, and -3.31 for temperatures 25, 37.5 and 50 °C, respectively, are in poor agreement with Couturier's (1986) data (log $K_5 = -3.72, -3.33$, and -3.10). At 50 °C, disagreement between these two sets of data is 0.21 log unit, but it increases to 0.45 log unit at 25 °C. This deviation may be caused by error in extrapolating the results of the present study, or by overestimation of the stability of $Al(OH)_3F^-$ in Couturier (1986). Besides, extrapolation of Couturier's (1986) data does not enable accurate calculation of Al speciation at higher temperatures. For example, extrapolation of the stability constant of $Al(OH)_3F^-$ given in Couturier (1986) gives Al concentrations up to two times and five times higher than those measured in the presence study at 90–200 and 300 °C, respectively. It should be noted that in Couturier's (1986) study, determination of Al–F complex stoichiometry from experimental data was impossible due to the small effect of
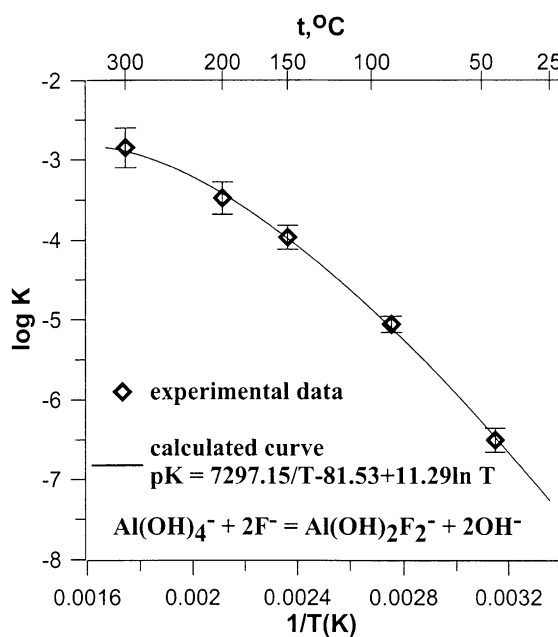

Fig. 5. Dependence of experimental (points) and calculated (line) values of the logarithms of the equilibrium constant for reaction (3) on the reciprocal temperature. The solid line represents a fit to the experimental data using Eq. (7).

Table 4
Thermodynamic parameters for the reaction (4): $Al(OH)_4^- + 2F^- = Al(OH)_2F_2^- + 2OH^-$

T (°C)	$\log K_{(4)}$	$\Delta_r G°$ (kJ/mol)	$\Delta_r H°$ (kJ/mol)	$\Delta_r S°$ (J/mol K)
25	− 7.26	41.46	75.28	113.4
50	− 6.28	38.84	69.88	96.0
100	− 4.88	34.84	59.07	64.9
150	− 3.98	32.28	48.26	37.8
200	− 3.42	31.01	37.46	13.6
250	− 3.08	30.88	26.65	− 8.1
300	− 2.90	31.78	15.84	− 27.8

fluorine on the measured e.m.f. before precipitation of a solid phase. Therefore, as the formation of $Al(OH)_3F^-$ is not certain, even at low temperatures, we prefer to assume that $Al(OH)_2F_2^-$ was the only Al–F complex formed at all the temperatures of this study.

4. Thermodynamic functions for formation of $Al(OH)_2F_2^-$

The values of $\log K_4$ listed in the first column of Table 3 are plotted against the reciprocal temperature in Fig. 5. Despite that reaction (4) is isocoulombic, the dependence of $\log K_4$ on $1/T(K)$ is not linear which implies $\Delta_r C_p^0 \neq 0$. Experimental values of $\log K_5$ were fit to:

$$pK = 7297.15/T(K) - 81.53 + 11.29 \cdot \ln T(K), \quad (7)$$

which is consistent with $\Delta_r C_p^0 = \text{constant}$. The reaction enthalpy and entropy were obtained by differentiation of Eq. (7) with respect to T, and the values of these thermodynamic parameters are given in Table 4 from 25 to 300 °C.

5. Conclusions

Boehmite and gibbsite solubility measurements carried out in NH_3-NH_4Cl+(NaCl) alkaline fluoride bearing solutions at temperatures at 300 °C have been used to quantify Al–F complexation in neutral to alkaline conditions. A single complex, $Al(OH)_2F_2^-$ was found to dominate Al speciation at the experimental conditions of this study. Stability of this species increases with temperature and the log K of the reaction

$Al(OH)_4^- + 2F^- = Al(OH)_2F_2^- + 2OH^-$ increases from − 7.26 at 25 °C to − 2.86 at 300 °C. Results obtained in the present study, together with corundum solubility data in HF solutions reported in Zaraisky (1994), suggest that Al mobility is greatly enhanced by the presence of mixed hydroxide fluoride complexes in near-neutral hydrothermal solutions.

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