

Potentiometric Study of Aluminium-Fluoride Complexation Equilibria and Definition of the Thermodynamic Model

M.S. Corbillon · M.A. Olazabal · J.M. Madariaga

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Abstract Complexation constants of the $\text{Al}^{3+}/\text{F}^-$ system were determined at different ionic strengths in a NaClO_4 (1.0, 2.0 and 3.0 $\text{mol}\cdot\text{dm}^{-3}$) ionic medium by means of a potentiometry using two electrode systems: an ion fluoride selective electrode as well as a glass electrode. All the experimentation was performed at 25 °C. The main species in the complexation equilibria were determined as AlF^{2+} , AlF_2^+ , AlF_3^0 , AlF_4^- , AlF_5^{2-} and AlF_6^{3-} . The differences found in the complexation constants for the ionic strength considered were explained by the different behavior of the interaction parameters for the AlF_n^{3-n} species. These parameters were calculated using the Modified Bromley's Methodology (MBM). The corresponding thermodynamic quantities were also determined. From all the results obtained, it can be concluded that pH, fluoride concentration and ionic strength influenced the distribution of the fluoride-aluminium complexes.

Keywords Aluminium fluoride complexation · Thermodynamic model · Interaction parameters

1 Introduction

The presence of fluorine compounds in natural waters has always been an important issue due to its potential toxicity. The main source of fluoride in water is not from natural origins but rather from industrial activities that have increased its level in natural waters as well as in soils and sediments. High-fluoride waters or addition of fluoride compounds to fluoridate natural waters for public consumption have been demonstrated to be a problem in conventional water treatment plants when aluminium is used as a coagulant because of turbidity and a residual aluminium increase [1]. These are the negative impacts of fluoride as a function of both pH (increases at $\text{pH} < 8$) and aluminium concentration (formation of $\text{Al}^{3+}/\text{F}^-$ complexes).

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Industries working with fluoride are forced to keep tight control of the total fluoride in residual water as well as in the production processes in order to minimize the release of fluoride compounds. Several methods have been introduced in recent years to treat fluoride-based industrial waste waters such as the addition of calcium and aluminium [2] or the use of electrolysis with aluminium electrodes [3], whereas methods based on phytoremediation techniques have been evaluated recently and found to have potential application because the uptake of fluoride is favored by the formation of aluminium complexes [4].

The aluminium industry also releases fluoride to the environment as gaseous species that are deposited in soils. Recently work performed in NW Spain (Galicia) involved measurements of water-extractable fluoride at two soil depths in a 3.5 km radius around an aluminium smelter factory and found a range of 13–140 mg·kg⁻¹ depending on both depth and distance [5]. When fluoride impacts the soil, some of the interactions with the solid phases are those with aluminium containing minerals, which are of the most critical for fluoride mobility, although the mechanisms controlling such mobility are not well understood, but suggest the importance of the Al³⁺/F⁻ complexes [6–8].

Plants cultivated in fluoride-rich soils incorporate both aluminium and fluoride [9]. Bio-accessibility experiments using such plants (different tea plants) with simulated gastric juices have shown the fluoro-aluminium species to be the dominant ones [9]. Aluminium fluoride complexes, specially AlF₄⁻, have a great impact on human physiology, stimulating various guanosine nucleotide binding proteins and inhibiting P-type ATPases [10]. Based on many studies, which utilize Al³⁺/F⁻ complexes in laboratory investigations, Strunecka and Patocka [11] suggest the importance of such complexes in stimulating impairment of homeostasis, degeneration and death of cells.

In all those examples, the Al³⁺/F⁻ complexes may play a critical role. There are other studies performed on other matrices like rainwater [12] and crustal fluids [13] where the F–Al speciation is essential to understand the processes. However, the inadequate Al³⁺/F⁻ chemical models do not let us extrapolate easily through the different conditions for both natural systems [1, 4, 6, 8] and biological fluids [14]. Several authors have studied aluminium-fluoride complexation equilibria, although most of them give stability formation constants for AlF²⁺, AlF₂⁺, AlF₃⁰, AlF₄⁻, not considering the last ones (AlF₅²⁻ and AlF₆³⁻). The main reason for this lack of information is the difficulty to quantify the formation of these species, because they give similar stability constant values and maybe because inadequate experimental techniques have been used. Taking into account that the ionic radius of fluoride ion is lower than the corresponding radius of water ($r_{F^-} = 1.33 \text{ \AA}$ [15], $r_{H_2O} = 1.39 \text{ \AA}$ [16]), fluoride ion can complete the octahedral coordination of aluminium giving the AlF₆³⁻ species.

The more complete work found in the literature is from Agarwal and Moreno [17] for KNO₃ at different ionic strengths ($0 < I \leq 0.5 \text{ mol}\cdot\text{dm}^{-3}$) and from Baumann [18] for NH₄NO₃ medium ($0 < I \leq 0.3 \text{ mol}\cdot\text{dm}^{-3}$), in which four complexes have been determined by potentiometry. In 1982 Katorina [19] determined the formation of six fluoro-complexes in aqueous NH₄NO₃ by the ISE potentiometric technique at different ionic strengths (0.2, 0.5 and 1.0 mol·dm⁻³). However, they concluded that there was no dependence of the complexation formation on ionic strength, which is improbable considering the charge of the ions present in the system. Perhaps an inappropriate knowledge of the fluoride ISE behavior [20] was a key factor in obtaining these unreliable Al³⁺/F⁻ formation constant values.

In this paper a systematic study of Al³⁺/F⁻ complexation is presented using H⁺ and F⁻ ISE electrodes at different ionic strengths in aqueous NaClO₄ at 25 °C in order to construct a thermodynamic model of the system.

A well-defined thermodynamic model should contain information about the chemical equilibria with the corresponding thermodynamic formation constant values as well as providing a way to estimate the activity coefficients of all the species as a function of the

chemical composition of the medium. The thermodynamic model of the hydrolytic species of aluminium has been defined in a previous study [21] and this work extends that chemical model to the complexation of aluminium with fluoride.

In order to overcome the problem of the effect of the chemical composition on the activity coefficients for all the species, the Modified Bromley's Methodology has been used. The great achievement of the equation proposed by Bromley for the estimation of the dependence of the activity coefficient on ionic strength is the use of only one interaction parameter for each ionic pair, allowing us to interpolate up to 6 mol·dm⁻³ ionic strength [22]. The calculation strategy to create the thermodynamic model [23] for situations where a central cation is coupled to monodentate ligands that can fill the maximum number of available coordination positions [24] will be used in this work.

2 Experimental

2.1 Reagents and Solutions

All reagents were of analytical grade with purities always greater than 99%, and were used without further purification. All solutions were prepared in fresh Milli-Q water.

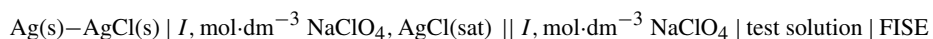
The ionic medium was sodium perchlorate (Fluka p.a.) whose concentrations were determined gravimetrically after evaporation of aliquots of the stock solutions at 110 °C.

The stock solutions of aluminium perchlorate, Al(ClO₄)₃ · 9H₂O (Aldrich p.a.), were standardized by titration with EDTA (Scharlau 0.1% mol·dm⁻³) and ZnO (Merck p.a.) with xylenol orange as an indicator [25].

NaOH (Merck p.a.) solutions were prepared under a N₂ atmosphere to avoid CO₂ contamination. Stock solutions of perchloric acid (Fluka p.a.) were used and their concentrations were standardized against tris(hydroxymethyl)aminomethane (Merck p.a.) using bromocresol green as the indicator [25]. Sodium fluoride, NaF Merck (p.a.), standard fluoride solution, Merck (1000 ± 2) mg·dm⁻³ was also used.

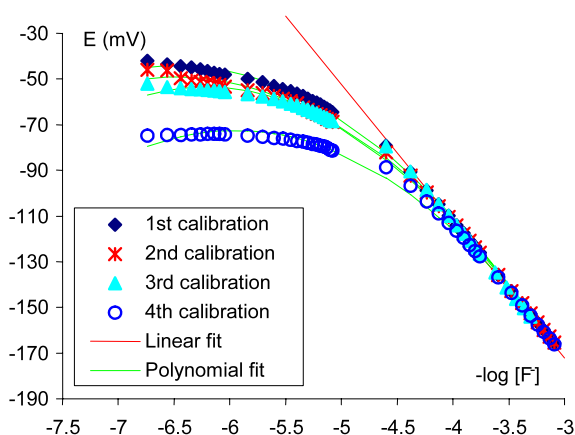
2.2 Apparatus

Potentiometric titrations were carried out in an automated system, developed in our laboratory [26]. The experiments were performed in a constant temperature oil bath at (25.0 ± 0.1) °C. In order to avoid CO₂ contamination, nitrogen pre-saturated with water from the same medium and ionic strength was continuously bubbled through the solutions and magnetic stirring was always employed. The potentiometric titrations were performed by measuring simultaneously the free proton concentration as well as the free fluoride concentration. The experimental set up consisted of a combined glass electrode which was hydrofluoric acid resistant (Crison model 52–06), a selective fluoride electrode (Radiometer F1052F) and a double-junction reference electrode (Ag(s)/AgCl(s) Orion model 90–02) as shown in the following schemes:



The electrodes were connected to a preamplifier in order to adapt the electric signal from the electrodes to the Hewlett-Packard VXI E1326B voltmeter. Measurements precisions of ±0.1 mV were achieved for both electrode systems. The automated titrant additions were

Fig. 1 Plot of the potential as a function of $[F^-]$ given by the fluoride selective electrode in successive titrations



performed with a Metrohm Dossimat 725 burette (precision $\pm 5 \mu\text{L}$) connected to a computer.

Taking into account the predominance of fluoride complexes at very acidic pH and the presence of hydrofluoric acid in solution, all the experiments were performed using hydrofluoric acid resistant materials, including Teflon cells as containers of the test solutions.

2.3 Experimental Procedure

Due to the impossibility of calibrating the electrode system in the same titration procedure, each titration was performed in three steps: the first step was to calibrate the glass electrode; the second step was to calibrate the fluoride selective electrode; and finally the third step was to perform the aluminium-fluoride titration.

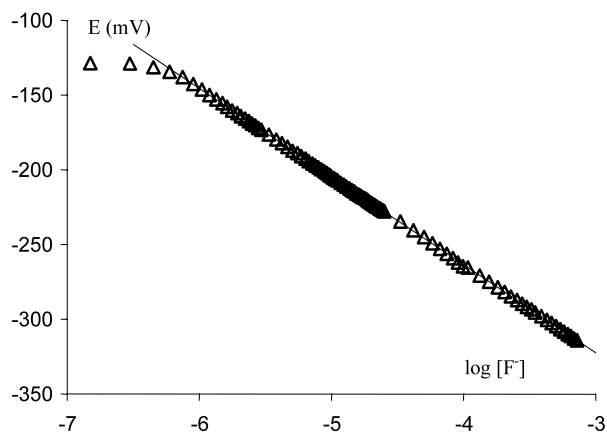
Glass Electrode Calibration The glass-electrode calibration was performed by a Gran titration at the corresponding ionic strength [27].

Fluoride ISE Calibration After the ionic medium titration was finished, (end of the first step attaining neutral pH), additions of NaF were performed in the 10^{-7} to $10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ range of fluoride concentration to measure the fluoride response (second step). The results obtained for the fluoride ion selective electrode calibration are plotted in Fig. 1. Two well-defined zones are observed, one with a convex curvature, which could be fitted by a polynomial function at F^- concentrations $C < 10^{-4.5}$ and another linear region, corresponding to Nernstian behavior, as the $[F^-]$ increases. When successive titrations were performed, the sensitivity in the non-linear zone was lost.

Despite the decrease in sensitivity at low fluoride concentrations, the sensitivity of electrode recovered after aluminium addition. This fact is mentioned in the literature by LaZeter and Hodges [28] and it can be observed in Fig. 2. In fact, the Nernstian response of the F^- ISE electrode ($E = E^0 + g \log_{10}[F^-]$) is extended from less than $10^{-6} \text{ mol}\cdot\text{dm}^{-3}$ until $10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ free F^- concentration. Therefore, a Nernstian response has been considered for both electrodes.

Aluminium-Fluoride Complexation Titrations The solution obtained at the end of the F^- ISE calibration was used to perform the complexation titrations after addition of the appropriate aluminium concentration. In order to avoid $\text{Al}(\text{OH})_3$ precipitation, HClO_4 acid

Fig. 2 Detection limit of FISE in the presence of $C_{Al} = 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$



was added before that of aluminium to get the $C_{Al}/C_F \approx 1$ relation; finally the titration was performed using aqueous NaF as titrant and measuring the potential value with both the glass electrode as well as the fluoride ion selective electrode. Each titration was performed at constant aluminium concentration. The $\text{Al}(\text{ClO}_4)_3$ concentrations used were 5×10^{-4} , 1×10^{-3} and $2 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$. For each titration the relationship C_{Al}/C_F was studied from 1 : 1 to 1 : 10. At least two titrations were performed using the same experimental conditions.

3 Results

The experimental data obtained from the potentiometric titrations were transformed into (Z , pF) data. The average number of fluoride ions bound to each aluminium can be calculated from:

$$Z = \frac{C_F - [\text{F}^-] - \sum_j [\text{HF}_j]}{C_{Al}} \quad (1)$$

where C_F and C_{Al} are the analytical concentrations of fluoride and aluminium, respectively, and $[\text{F}^-]$ is the free fluoride concentration obtained from the E_F values.

$$[\text{F}^-] = 10^{(E_F - E_F^0)/g} \quad (2)$$

and

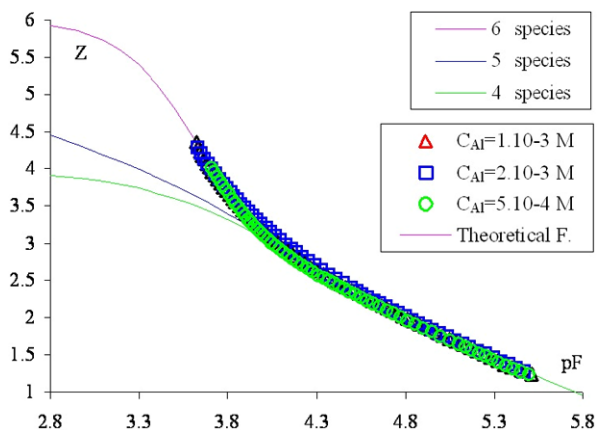
$$\sum_j [\text{HF}_j] = \beta_1 [\text{H}^+][\text{F}^-] + 2\beta_2 [\text{H}^+][\text{F}^-]^2 \quad (3)$$

being

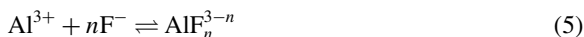
$$[\text{H}^+] = 10^{(E_H - E_H^0)/g} \quad (4)$$

Figure 3 shows, as an example, the experimental Z versus pF data at $2.0 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 . As can be seen, values for $Z > 4.5$ were not obtained, thus some doubt can arise from this fact. In order to clarify the importance of the $\text{Al}^{3+}/\text{F}^-$ complexes for the whole set of data collected for each titration, a graphical treatment was developed.

Fig. 3 The Z versus pF function showing experimental data and (—) theoretical curves considering four, five or six fluoro complexes in $2.0 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 . The experimental data were collected at three C_{Al} values



The complexation equilibria between Al^{3+} and F^- can be represented by the general equilibrium:



and its corresponding stoichiometric constant:

$$\beta_n = \frac{[\text{AlF}_n^{3-n}]}{[\text{Al}^{3+}][\text{F}^-]^n} \quad (6)$$

As it can be seen, all the data for different total concentrations of aluminium are fitted by the same theoretical Z function. Thus, it can be concluded that polynuclear aluminium species are not formed in the concentration range used in this work.

In these conditions the mass balance equations for both components can be written as:

$$C_{\text{F}} = [\text{F}^-] + \sum_j j[\text{HF}_j] + \sum_n n[\text{AlF}_n] \quad (7)$$

$$C_{\text{Al}} = [\text{Al}^{3+}] + \sum_{r,s} r[\text{Al}_r(\text{OH})_s] + \sum_n [\text{AlF}_n] \quad (8)$$

The aluminium hydroxo complexes can be defined, in general, as

$$[\text{Al}_r(\text{OH})_s] = \beta_{r,s}[\text{Al}^{3+}]^r[\text{OH}^-]^s \quad (9)$$

Taking into account the C_{Al} values used and the pH values obtained from the potentiometric titrations, the presence of polynuclear aluminium hydroxo complexes were considered to be negligible; thus Eq. 9 transforms into:

$$[\text{Al}(\text{OH})_s] = \beta_{1,s}[\text{Al}^{3+}][\text{OH}^-]^s \quad (10)$$

Introducing Eqs. 7 and 8 together with the constants in Eqs. 6 and 10, the calculated Z function in Eq. 1 is obtained for the six $\text{Al}^{3+}/\text{F}^-$ complexes

$$Z = \frac{\beta_1[\text{F}^-] + 2\beta_2[\text{F}^-]^2 + \dots + 6\beta_6[\text{F}^-]^6}{1 + \beta_{11}[\text{OH}^-] + \beta_{12}[\text{OH}^-]^2 + \beta_1[\text{F}^-] + \beta_2[\text{F}^-]^2 + \dots + \beta_6[\text{F}^-]^6} \quad (11)$$

Table 1 Values of stoichiometric formation constants of aluminium-fluoro complexes at different ionic strengths in NaClO₄ at 25 °C

<i>I</i> (mol·dm ⁻³)	1.0	2.0	3.0
log ₁₀ β ₁	6.07 ± 0.02	6.20 ± 0.02	6.40 ± 0.04
log ₁₀ β ₂	11.06 ± 0.02	11.48 ± 0.04	12.07 ± 0.07
log ₁₀ β ₃	14.98 ± 0.04	15.80 ± 0.06	16.76 ± 0.07
log ₁₀ β ₄	18.12 ± 0.05	19.63 ± 0.06	20.89 ± 0.05
log ₁₀ β ₅	21.17 ± 0.06	22.46 ± 0.04	24.01 ± 0.04
log ₁₀ β ₆	24.50 ± 0.04	26.84 ± 0.03	28.98 ± 0.07
σ (E _B), (mV)	0.192	0.153	0.287
U _{abs}	3.88	4.05	4.66

A similar *Z* function can be obtained for five (AlF²⁺ to AlF₅²⁻) or four (AlF²⁺ to AlF₄⁻) complexes. The best theoretical functions for four, five or six Al³⁺/F⁻ complexes are plotted in Fig. 3 together with some experimental data for the same ionic strength. As seen, four and five species are not enough to explain the whole experimental data set.

The graphical fit of the data, like those shown in Fig. 3, by Eq. 11 gave the first idea of the magnitude for each AlF_{*n*}^{3-*n*} formation constant. In order to refine the stoichiometric formation constant obtained by the graphical treatment, a numerical treatment was carried out with NYTIT [29] of the LETAGROP program, because this program can be used for each experimental potential value collected by the two different electrodes. The experimental data have been adjusted by minimizing the sum of the squares of the deviations in ISE potential for all the experimental points:

$$U_{E_B} = \sum_{N_p} (E_{B,calc} - E_{B,exp})^2 \quad (12)$$

Table 1 summarizes the results obtained numerically at the different ionic strengths studied. As can be seen, the standard deviation for the whole fit, σ (E_B), is twice the experimental repeatability indicating the goodness of both the experimental data and the model of the equilibria used to explain them.

The goodness of the fit is also shown in Fig. 3 where the experimental data are compared with the theoretical Eq. 11 computed with the formation constant values summarized in Table 1 at 2.0 mol·dm⁻³ ionic strength.

Thermodynamic Model

In order to build a suitable thermodynamic model, it is necessary to have as many stoichiometric stability constant values at different ionic strengths as possible. In this way the Modified Bromley's Methodology [22–24] has been used to estimate the thermodynamic constants as well as the interaction parameters for all the species present in the chemical system.

Considering the general equilibrium represented by Eq. 5, the next relation can be established between thermodynamic and stoichiometric constant:

$${}^0\beta_n = \frac{\{\text{AlF}_n^{3-n}\}}{\{\text{Al}^{3+}\}\{\text{F}^-\}^n} = {}^I\beta_n \left(\frac{\gamma_{\infty_n^{3-n}}}{\gamma_{\text{Al}^{3+}} \gamma_{\text{F}^-}^n} \right) \quad (13)$$

where γ_{*i*} is the molar activity coefficient of species *i*.

According to the MBM, the individual molar activity coefficient of any charged species can be calculated as:

$$\log_{10} \gamma_M = -\frac{0.5115 z_M^2 I^{1/2}}{1 + I^{1/2}} + F_i = z_M^2 D + F_i \quad (14)$$

where F_i ,

$$F_i = \sum_x \dot{B}_{MX} (|z_M| + |z_X|)^2 \frac{[X]}{4} \quad (15)$$

where z_M is the ionic charge of species M, and X represents all the counter ions present in solution, and I is the molar ionic strength.

The term \dot{B}_{MX} is defined as:

$$\dot{B}_{MX} = \frac{(0.06 + 0.6 B_{MX}) |z_M z_X|}{\left(1 + \frac{1.5}{|z_M z_X|} I\right)^2} + B_{MX} \quad (16)$$

where \dot{B}_{MX} is the so-called Bromley's interaction parameter [30] and the corresponding activity coefficient for the uncharged species can be expressed by:

$$\log_{10} \gamma_i = \sum_{XY} S_{(i,XY)} I_{XY} \quad (17)$$

As an example, for the equilibrium:



the stoichiometric complexation constant can be rewritten as a function of the thermodynamic constant and the activity coefficients

$${}^0\beta_n = \frac{\{\text{AlF}^{2+}\}}{\{\text{Al}^{3+}\}\{\text{F}^-\}} = {}^I\beta_1 \left(\frac{\gamma_{\text{AlF}^{2+}}}{\gamma_{\text{Al}^{3+}} \gamma_{\text{F}^-}} \right) \quad (19)$$

or in the logarithmic form

$$\log_{10} {}^I\beta_1 = \log_{10} {}^0\beta_1 + \log_{10} \gamma_{\text{Al}^{3+}} + \log_{10} \gamma_{\text{F}^-} - \log_{10} \gamma_{\text{AlF}^{2+}} \quad (20)$$

where γ denotes the molar activity coefficient.

According to the MBM, the individual activity coefficients of the charged species can be calculated as:

$$\log_{10} \gamma_{\text{AlF}^{2+}} = 4D + F_1 \quad (21)$$

$$\log_{10} \gamma_{\text{Al}^{3+}} = 9D + F_2 \quad (22)$$

$$\log_{10} \gamma_{\text{F}^-} = D + F_3 \quad (23)$$

where

$$D = -\frac{0.5115 I^{1/2}}{1 + I^{1/2}} \quad (24)$$

$$F_1 = \left(\frac{(0.06 + 0.6B_{\text{AlF}_2^+, \text{ClO}_4^-})2}{(1 + 0.75I)^2} + B_{\text{AlF}_2^+, \text{ClO}_4^-} \right) \frac{9}{4} [\text{ClO}_4^-] \tag{25}$$

$$F_2 = \left(\frac{(0.06 + 0.6B_{\text{AlF}_3^+, \text{ClO}_4^-})3}{(1 + 0.5I)^2} + B_{\text{AlF}_3^+, \text{ClO}_4^-} \right) 4[\text{ClO}_4^-] \tag{26}$$

$$F_3 = \left(\frac{(0.06 + 0.6B_{\text{F}^-, \text{Na}^+})}{(1 + 1.5I)^2} + B_{\text{F}^-, \text{Na}^+} \right) [\text{Na}^+] \tag{27}$$

Then,

$$\log_{10} {}^I\beta_1 = \log_{10} {}^0\beta_1 + 6D - F_1 + F_2 + F_3 \tag{28}$$

For this system, the other equilibria correlation functions are:

$$\log_{10} {}^I\beta_2 = \log_{10} {}^0\beta_2 + 10D - F_4 + F_2 + 2F_3 \tag{29}$$

$$\log_{10} {}^I\beta_3 = \log_{10} {}^0\beta_3 + 12D - F_5 + F_2 + 3F_3 \tag{30}$$

$$\log_{10} {}^I\beta_4 = \log_{10} {}^0\beta_4 + 12D - F_6 + F_2 + 4F_3 \tag{31}$$

$$\log_{10} {}^I\beta_5 = \log_{10} {}^0\beta_5 + 10D - F_7 + F_2 + 5F_3 \tag{32}$$

$$\log_{10} {}^I\beta_6 = \log_{10} {}^0\beta_6 + 6D - F_8 + F_2 + 6F_3 \tag{33}$$

where F_1 includes the parameter $B_{\text{AlF}_2^+, \text{ClO}_4^-}$

F_2 includes the parameter $B_{\text{AlF}_3^+, \text{ClO}_4^-} = (0.100 \pm 0.009) \text{ dm}^3 \cdot \text{mol}^{-1}$ taken from [21]

F_3 includes the parameter $B_{\text{F}^-, \text{Na}^+} = (0.0040 \pm 0.0002) \text{ dm}^3 \cdot \text{mol}^{-1}$ taken from [21]

F_4 includes the parameter $B_{\text{AlF}_2^+, \text{ClO}_4^-}$ that must be calculated

F_5 includes the parameter $S_{\text{AlF}_3, \text{NaClO}_4}$

F_6 includes the parameter $B_{\text{AlF}_4^-, \text{Na}^+}$

F_7 includes the parameter $B_{\text{AlF}_5^{2-}, \text{Na}^+}$

F_8 include the parameter $B_{\text{AlF}_6^{3-}, \text{Na}^+}$.

The thermodynamic constants and interaction parameters were calculated numerically by means of the NLREG [31] program using the previous equations. The values obtained are summarized in Table 2 and the fits for the six equilibrium constants are shown in Fig. 4.

Table 2 Thermodynamic constants and interaction parameters in the molar scale for aluminium fluoro complexes determined by the MBM in NaClO₄ at 25 °C

Species	Therrnodynamic constants	Interaction parameters (dm ³ ·mol ⁻¹)
AlF ²⁺	6.72 ± 0.07	$B_{\text{AlF}_2^+, \text{ClO}_4^-} = 0.029 \pm 0.013$
AlF ₂ ⁺	12.08 ± 0.06	$B_{\text{AlF}_2^+, \text{ClO}_4^-} = -0.423 \pm 0.029$
AlF ₃	16.09 ± 0.06	$S_{\text{AlF}_3, \text{NaClO}_4} = -0.872 \pm 0.029$
AlF ₄ ⁻	18.64 ± 0.07	$B_{\text{AlF}_4^-, \text{Na}^+} = -1.391 \pm 0.039$
AlF ₅ ²⁻	20.79 ± 0.07	$B_{\text{AlF}_5^{2-}, \text{Na}^+} = -0.600 \pm 0.013$
AlF ₆ ³⁻	21.69 ± 0.08	$B_{\text{AlF}_6^{3-}, \text{Na}^+} = -0.490 \pm 0.007$

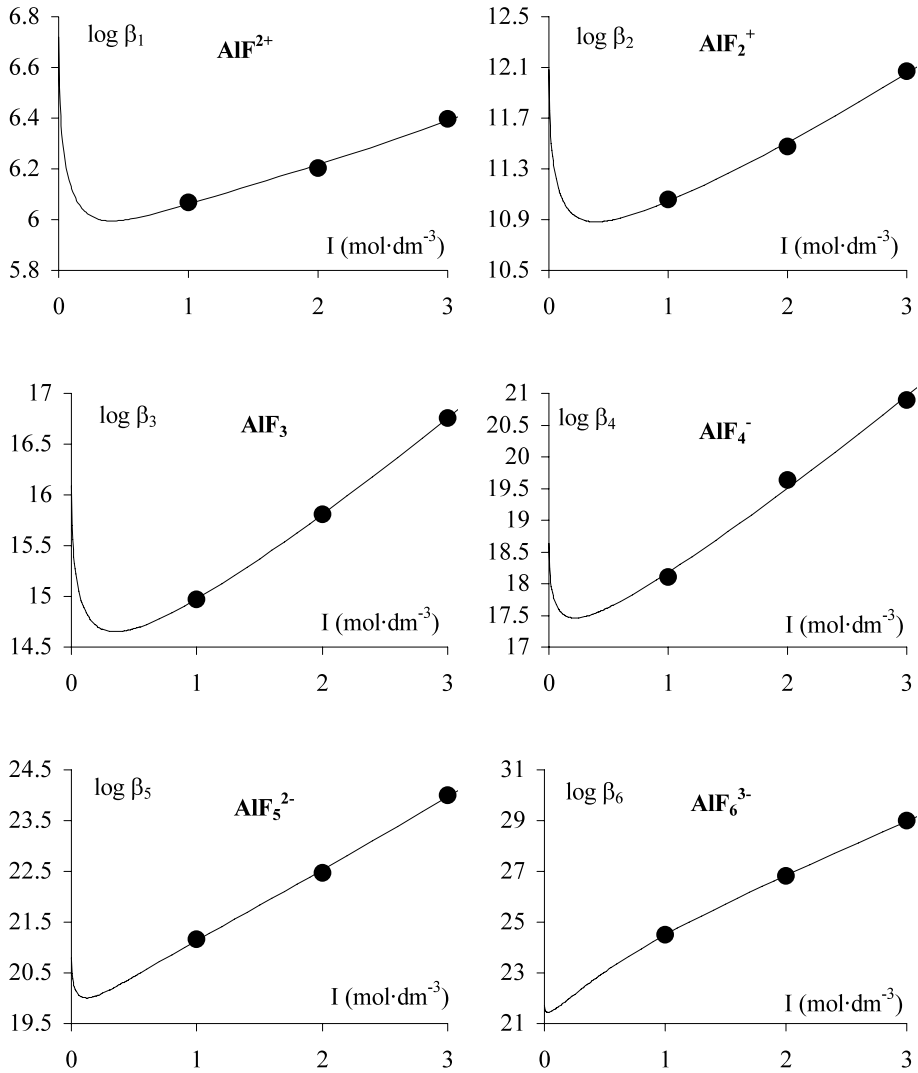


Fig. 4 Variation of the stoichiometric formation constants for all the AlF_n^{3-n} species in the $\text{Al}^{3+}/\text{F}^-$ chemical system as a function of the ionic strength (NaClO_4)

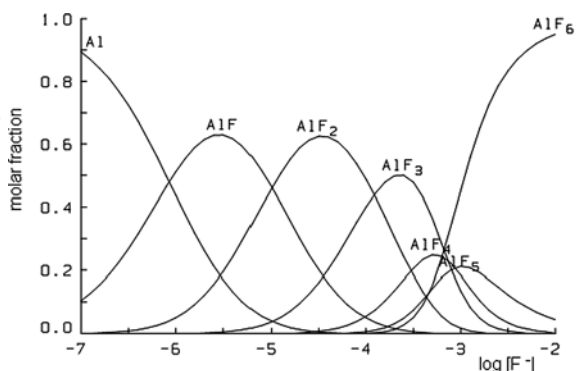
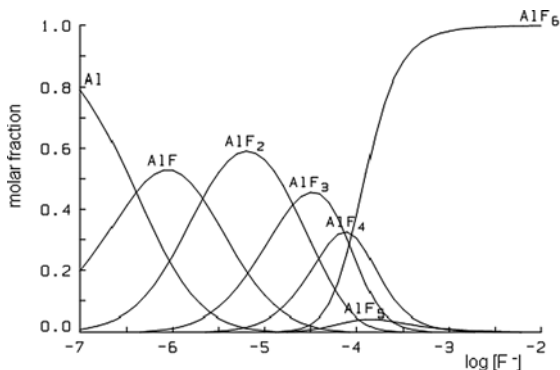
The correlation was performed on the molal scale. Previously, the stoichiometric constant values on the molal scale were calculated following the procedure described elsewhere [23]. The thermodynamic constant values and interaction parameters on the molal scale were calculated using the same methodology that was used for the data on the molar scale. The adjusted values are collected in Table 3. The known interaction parameters calculated in a previous work [21] on the molal scale were:

$$B_{\text{Al}^{3+}, \text{ClO}_4^-} = (0.048 \pm 0.013) \text{ kg}\cdot\text{mol}^{-1}$$

$$B_{\text{F}^-, \text{Na}^+} = (0.0042 \pm 0.0008) \text{ kg}\cdot\text{mol}^{-1}$$

Table 3 Thermodynamic constants and interaction parameters on the molal scale for the aluminium fluoro complexes by MBM in a NaClO₄ medium at 25 °C

Species	Thermodynamic constants	Interaction parameters (kg·mol ⁻¹)
AlF ²⁺	6.72±0.08	$B_{\text{AlF}^{2+}, \text{ClO}_4^-} = -0.062 \pm 0.017$
AlF ₂ ⁺	12.08±0.07	$B_{\text{AlF}_2^+, \text{ClO}_4^-} = -0.582 \pm 0.042$
AlF ₃	16.09±0.07	$S_{\text{AlF}_3, \text{NaClO}_4} = -0.963 \pm 0.043$
AlF ₄ ⁻	18.63±0.08	$B_{\text{AlF}_4^-, \text{Na}^+} = -1.402 \pm 0.047$
AlF ₅ ²⁻	20.79±0.08	$B_{\text{AlF}_5^{2-}, \text{Na}^+} = -0.599 \pm 0.017$
AlF ₆ ³⁻	21.69±0.09	$B_{\text{AlF}_6^{3-}, \text{Na}^+} = -0.471 \pm 0.008$

Fig. 5 Distribution diagram of Al/F species as a function of log₁₀[F⁻], where $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$, NaClO₄, $C_{\text{Al}} = 8.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ and pH = 2.5**Fig. 6** Distribution diagram of Al/F species as a function of log₁₀[F⁻], where $I = 3.0 \text{ mol}\cdot\text{dm}^{-3}$, NaClO₄, $C_{\text{Al}} = 8.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ and pH = 2.5

The species distribution diagrams for the Al³⁺/F⁻ system at different ionic strengths are plotted in Figs. 5 and 6. The strong influence of ionic strength can be observed. The value of [F⁻] where AlF₆³⁻ is formed quantitatively decreases as the ionic strength increases (more than ten times when I changes from 1.0 to 3.0 mol·dm⁻³).

From this work it can be concluded that the ionic strength effect has probably the strongest influence on the distribution diagram of the species, and must be considered carefully in order to develop any further analytical method or chemical procedure. For example, high ionic strength must be used to determine aluminium by a complexometric titration

with fluoride, aluminium is more easily exchanged by anionic resins as AlF_6^{3-} at higher ionic strengths and is quantitatively eluted at the lower ones (even with water).

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