Aggregation and Dissociation of Aqueous Al_{13}^{7+} Induced by Fluoride Substitution

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Supporting Information

ABSTRACT: The ϵ -Keggin ion $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (ϵ -K Al_{13}^{7+}) is a double-edged sword, because it commonly acts as a toxic component toward aquatic organisms, but also is considered to be an effective coagulant. Gaining deep insight into the transformation of ϵ -K Al_{13}^{7+} in the presence of coexisting ligands would have significant implications for water environmental science, as well as for practical water purification. The aggregation and dissociation of aqueous Al_{13}^{7+} induced by fluoride (F^-) substitution were herein investigated using nuclear magnetic resonance, electrospray ionization–mass spectrometry, and theoretical calculations. The F^- substitution on η - OH_2 sites was extremely fast, reducing the charge of ϵ -K Al_{13}^{7+} so that the repulsive force between fluorinated Al_{13} species was immediately reduced. Consequently, fluorinated Al_{13} aggregated, with the formula $[\text{Al}_{13}\text{F}_5]^{2+}$, which was demonstrated by calculating the Gibbs free energy changes ($\Delta_r G$) of the substitution reactions involved. Moreover, the replacement of η - OH_2 with F^- weakened the strength of $\text{Al}-\text{OH}^{\text{a/b}}$ bonds and thus prompted the replacement of μ - $\text{OH}^{\text{a/b}}$ with F^- . In addition, fluorination prompted $[\text{Al}_{13}\text{F}_5]^{2+}$ to dissociate to oligomers.

INTRODUCTION

Aluminum (Al) is the most abundant metal in Earth's geological environment, and research on Al chemistry plays an important part in the fields of geoscience, water and soil environments, and ecology.^{1–3} A variety of Al species exist, including solute molecules (Al monomers, Al polymers) and hydroxide precipitates (e.g., gibbsite),^{4–6} among which the ϵ -isomer Keggin $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (ϵ -K Al_{13}^{7+}) polymer has been demonstrated thermodynamically to be a crucial intermediate species in the transformation of aqueous Al to Al hydroxide precipitates.^{7,8} With multiple coordinated hydroxyl groups and high charges, the ϵ -K Al_{13}^{7+} structure includes 12 edge-shared AlO_6 octahedra in four sets of triple linked trimers around a central AlO_4 tetrahedron.^{9,10} The ϵ -K Al_{13}^{7+} polymer has been detected in watersheds polluted by mine drainage and acid rain^{11,12} and has a toxicity that is rather general and more virulent to plants and fishes than Al monomers.^{13–15} Previous studies have reported that ϵ -K Al_{13}^{7+} is a crucial component for mineral paragenesis and dissolution, as well as for sorption reactions at the solid–water interface,^{16,17} which regulate the transformation of ions in the geochemical environment.

Due to Lewis acid–base complexation and electrostatic interactions, coexisting ligands (fluoride, carboxylate, and natural organics)

strongly react with the Al_{13}^{7+} polymer, leading to the morphological transformation of both.^{18–20} The ubiquitous F^- can dissolve the ϵ -Keggin structure during water–rock interaction.²¹ The ϵ -K Al_{13}^{7+} polymer has been reported to be an effective component for coagulation and complexation of contaminants in water purification and soil remediation,^{22–24} and exhibits especially superior aqueous fluoride (F^-) removal efficiency compared to other aluminum species.²⁵ Therefore, the investigation on the interaction mechanism of ϵ -K Al_{13}^{7+} and F^- would be helpful not only to understanding the transformation and migration of Al_{13} and F in the geological environment but also to provide a basis for the application and regulation of Al polymers in water treatment, which has attracted wide attention from environmental researchers.

According to previous research, the hydroxyl coordination on the Keggin structure is divided into three types with different activities according to the configuration: outer binding water (η - OH_2), hydroxyl between two trimers (μ - OH^{a}), and hydroxyl

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between two Al in one trimer ($\mu\text{-OH}^b$), which are the binding sites for ligands.^{26,27} ^{19}F nuclear magnetic resonance (NMR) results confirmed that three types of hydroxyl coordination can be substituted by F^- at different reaction rates on $\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}$.⁷⁺²⁸ The substitution path involved the transfer of F to $\mu\text{-F}^{a/b}$ from $\eta\text{-F}$. In the meantime, based on the theoretical predictions, F-substitution of $\varepsilon\text{-K Al}_{13}^{7+}$ at $\mu\text{-OH}^a$, $\mu\text{-OH}^b$, and $\eta\text{-OH}$ sites decreased the reactivity at $\eta\text{-OH}_2$, and the structure was readily dissociated in solutions.²⁹ These $\text{Al}_{13}^{7+}\text{-F}$ theories provided us an ideal platform to gain deep insight into the processes of complexation, aggregation, and precipitation in the presence of Al in a complex natural water system, which is beneficial to polluted watershed remediation and drinking water treatment.

Combining experimental analysis and theoretical predictions, we herein focused on the study of the interaction mechanism between $\varepsilon\text{-K Al}_{13}^{7+}$ and F^- , to reveal the essential reactions involved in water environments and water purification. The transitions of Al species and F species during the reaction of $\varepsilon\text{-K Al}_{13}^{7+}$ and F^- , as well as the rates of F^- substitution on three different oxygen sites of $\varepsilon\text{-K Al}_{13}^{7+}$, were quantitatively investigated using liquid and solid magic-angle-spinning (MAS) NMR detection methods. In addition, the reaction products were characterized via electrospray ionization quadrupole–time of flight–mass spectrometry (ESI-TOF-MS), and their formation mechanisms were elucidated by combining experimental results and theoretical calculations. Finally, the environmental significance of the results was discussed.

■ EXPERIMENTAL SECTION

Preparation of $\varepsilon\text{-Keggin Al}_{13}^{7+}$ Solution. $\varepsilon\text{-K Al}_{13}^{7+}$ solution was obtained by purifying a polyaluminum chloride solution prepared with an electrolysis process.^{30–32} The ^{27}Al NMR (Bruker Avance^{III} 400, USA) spectrum of the prepared solution exhibits a peak at 63 ppm which is assigned to the $\text{Al}(\text{O})_4$ tetrahedral site of $\varepsilon\text{-K Al}_{13}$ and a peak at 0 ppm due to aluminum monomers (Figure S1). The percentages of $\varepsilon\text{-K Al}_{13}$ and monomers were 98.25% and 0.56%, respectively, which were quantified based on the areas of the signals.

Reaction of $\varepsilon\text{-K Al}_{13}^{7+}$ and F^- . Fluoride stock solutions (NaF, pH 6.0) were added into $\varepsilon\text{-K Al}_{13}$ solutions (pH 5.0) with two concentrations levels as the total Al, according to the F–Al molar ratios ($R_{\text{F:Al}}$) of 1:15, 2:15, 3:15, 4:15, 5:15, and 6:15, with rapid stirring at 20 °C for 2 h. In either polluted watersheds or drinking water treatment plants, the aqueous pH is around 6.5–7.0. Due to the similar Al–F complex reaction in the presence of Al_{13} , the coagulation performance of AlCl_3 almost maintained the same level in pH range from 5 to 7.^{25,33} To deep insight into $\text{Al}_{13}\text{-F}$ reaction mechanism, it was reasonable to slightly lower the pH value for the high-purity Al_{13} structure, so that it confirms the absence of interference from other Al species. Thus, the pH was herein maintained at ~ 5.0 . In the experiments, 0.1–0.6 mL of 8 mM or 0.5–3.0 mL of 0.8 M NaF solutions were added in 20 mL of 0.6 mM or 0.3 M $\varepsilon\text{-K Al}_{13}$ solution, respectively, and the pH values of the mixtures can be predicted to be 5.00–5.01 or 5.01–5.05. The actual pH values of 5.01–5.05 and 5.05–5.20 were a little higher than the predictions (Table S1), which was due to the release of hydroxyl ions during the reaction process. However, the pH value was still within the range compatible with the $\varepsilon\text{-K Al}_{13}$ species. The samples were filtered through ultrafiltration

membranes (3000 Da) to separate the filtrates and precipitates. The reaction products in the filtrates of low concentration samples (Al_T : 0.6 mM) were detected by ESI-TOF-MS (ACQUITY UPLC/Xevo G2 Q TOF, Waters, USA). In addition, the filtrates of high concentration samples (Al_T : 0.3 M) were qualitatively and quantitatively analyzed using $^{19}\text{F}/^{27}\text{Al}$ NMR (Bruker Avance^{III} 500, USA), and the precipitates were qualitatively analyzed using $^{27}\text{Al}/^{19}\text{F}$ MAS NMR. Inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2000 PerkinElmer, USA) and a Dionex 2000 ion chromatography system (ICS, Dionex 2000, USA) were used to determine the total Al and F concentrations in filtrates.

Concentration Changes of Fluorinated Sites. The changes of F^- substitution sites on the $\varepsilon\text{-K Al}_{13}^{7+}$ polymer during the reaction were evaluated by real-time ^{19}F NMR. To meet concentration requirements for rapid detection by ^{19}F NMR, the total Al concentration of $\varepsilon\text{-K Al}_{13}$ solutions was 0.3 M, and the F concentration was 0.02 M. The first spectrum was acquired at 4.5 min after adding fluoride, and NMR measurement was continued for 1057 min.

Zeta Potential Detection. Zeta potentials and the size distribution in the suspensions after $\text{Al}_{13}^{7+}\text{-F}^-$ reaction in 0.6 mM of Al_T were measured using dynamic light scattering (DLS, Zetasizer Nano ZS90, Malvern, USA), with 0.3–100 μm measurable size range. To maintain the ionic strength, 10 mM NaCl was added into the suspensions. The zeta potential was obtained from the measurement of the electrophoretic mobility according to Henry's equation (eq 1).³⁴ U/E is the electrophoretic mobility ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$), ζ is the zeta potential (V), ε is the solvent dielectric permittivity ($\text{kg m V}^{-2} \text{s}^{-2}$), η is the viscosity ($\text{kg m}^{-1} \text{s}^{-1}$), and $F(ka)$ is Henry's function (dimensionless). ε and η values were measured using a microwave network analyzer (Agilent N5224A, USA) and a viscometer (BrookField DV2TLV, USA), respectively. $F(ka)$ was set to 1.5.³⁵

$$\frac{U}{E} = \frac{2e\zeta F(ka)}{3\eta} \quad (1)$$

ESI-TOF-MS Analyses. The ESI-TOF-MS spectra were recorded on a micromass hybrid quadrupole time-of-flight mass spectrometer equipped with an electrospray ion source. Sodium formate solution was used to correct the mass spectra before the detection, and a leucine–enkephalin solution was used for real-time correction to ensure the accuracy of the mass spectrometry. All mass spectral data were performed in positive ion mode. The instrumental conditions were as follows: capillary voltage 3500.0 V, sample cone voltage 70 V (40, 60, and 150 V), extraction cone voltage 5 V, source temperature 120 °C, desolvation temperature 150 °C, cone gas (N_2) flow rate 300 L h^{−1}, and mass range 50–1000.^{36,37}

NMR Analyses. ^{27}Al and ^{19}F NMR were recorded on a Bruker Avance^{III} 500 spectrometer, with 130 and 470 MHz resonance frequencies, respectively. ^{27}Al NMR parameters were: repetition delay 2 s, frequency 130.3 MHz, scan width 39682.5 Hz, and number of scans 256. ^{19}F NMR parameters were: repetition delay 2 s, frequency 470.6 MHz, scan width 71428.6 Hz, and number of scans 128. NaAlO_2 (80 ppm) and NaSiF_6 (−129 ppm) solutions of known concentrations were employed as external standards for ^{27}Al NMR and ^{19}F NMR, respectively, acting as the references for chemical shifts and relative peak areas. The concentrations of fluorinated sites and Al species were calculated according to the functional relationships between the concentrations of a series of NaF

or AlCl_3 ($\text{pH} < 1$) solutions and their relative peak areas. The concentration of Al in Al_{13} form in solution equaled the concentration (as determined by peak area) of the signal at 63 ppm multiplied by 13.

Solid-state NMR was detected via the MAS technique. ^{27}Al MAS NMR was recorded on a Bruker Avance^{III} 400 (9.4 T) spectrometer with a 104 MHz resonating frequency. ^{19}F MAS NMR was recorded on a Bruker Avance^{III} 500 WB (11.75 T) spectrometer with a 471 MHz resonating frequency. The ^{27}Al MAS NMR parameters were: repetition delay 1 s, number of scans 128, spinning rate 13 kHz, and scan width 104 166 Hz. The ^{19}F MAS NMR parameters were: repetition delay 4 s, number of scans 1000, and spinning rate 25 kHz. ^{27}Al MAS NMR spectra and ^{19}F MAS NMR spectra were referenced to 1 M $\text{Al}(\text{NO}_3)_3$ (0 ppm) and CF_2 groups of PTFE (−122 ppm), respectively. The NMR spectra were fitted using Bruker TopSpin 3.2 with the CSA model, considering the sample spinning rate (25 000 Hz), isotropic chemical shift $\delta(\text{ISO})$, chemical shift anisotropy $\delta(\text{CSA})$, asymmetry factor $\eta(\text{CSA})$, and line broadening (LB). Three or four sites were fixed in the fitting process, and the intensity, $\delta(\text{iso})$, $\delta(\text{CSA})$, and $\eta(\text{CSA})$ were allowed to float individually in an iterative fashion until the fitting line matched the data.

COMPUTATIONAL METHODS

All of the calculations were carried out with the Gaussian 09 program.³⁸ Geometry optimization and frequency analysis were performed using the B3LYP functional^{39–41} and 6-31G* basis set. Single-point energies were calculated with the M06 functional⁴² and a basis set of 6-311+G(d,p) for all atoms. Solvation energy corrections were calculated using the SMD⁴³ model. In accordance with the experimental conditions, water was used as the solvent in the calculations. The Gibbs free energies reported include thermal corrections computed at 298.15 K.

Taking the F^- replacement of $\eta\text{-OH}_2$ of Al_{13}^{7+} as a model reaction, we performed single point energy calculations using three kinds of commonly used density functions to assess the accuracy of the selected method. The results are listed in Table S2 of the Supporting Information. The results indicated that the Gibbs free energy changes ($\Delta_r G$) obtained with the three kinds of functions for this model reaction were very close to each other, which confirmed that our conclusions were reliable based on the M06/6-311+G(d,p)/SMD(water)//B3LYP/6-31G(d) computed energies.

RESULTS AND DISCUSSION

Products of $\text{Al}_{13}^{7+}\text{-F}^-$ Complexation. The reaction of $\varepsilon\text{-K Al}_{13}^{7+}$ and F^- was studied by adding fluoride solution dropwise into prepared $\varepsilon\text{-K Al}_{13}$ solutions with total Al concentrations (Al_T) of 0.6 mM, which represented its real levels in natural water,^{20,44} polluted watersheds,¹² and coagulation processes^{45,46}. The molar ratios of initial F to Al ($R_{\text{F:Al}}$) were set to 1:15, 2:15, 3:15, 4:15, 5:15, and 6:15, respectively. The complexation products in the filtrates, obtained by ultra-filtration membrane separation, were examined by the ESI-TOF-MS instrument, which was influenced by the cone voltage. In contrast to insufficient ionization of the ion at low cone voltage (40 V), the higher cone voltage (150 V) caused the fragmentation of Al ions; thereby parts of Al species were not detected (Figure S2). Therefore, the optimum cone voltage was determined to be 70 V, for which the prepared $\varepsilon\text{-K Al}_{13}^{7+}$ solution mainly exhibited peaks of Al_{13} at m/z 249.3–213.2

($\text{AlO}_4\text{Al}_{12}\text{O}_{7+n}(\text{OH})_{20-2n}^{3+}$, $n = 0\text{--}4$, $[\text{Al}_{13}]^{3+}$) subtracting six in turn, and m/z 391.4–328.3 ($\text{AlO}_4\text{Al}_{12}\text{O}_{7+n}(\text{OH})_{15-2n}^{2+}$, $n = 0\text{--}7$, $[\text{Al}_{13}]^{2+}$) subtracting nine in turn, as shown in Figure 1a. These two groups of peaks are produced through deprotonation or changing two hydroxo groups to an oxo group during ionization processes.^{47,48}

After reaction, some new peaks appeared to the right of the original Al_{13} peaks when the $R_{\text{F:Al}}$ values were 1:15, 2:15, 3:15, 4:15, and 5:15, as illustrated in Figure 1b–f. The ionic strength of the sample with $R_{\text{F:Al}}$ 6:15 was extremely low, and no characteristic peaks were observed in the spectrum. Considering the mass differences between the new peaks and $[\text{Al}_{13}]^{2+}$ or $[\text{Al}_{13}]^{3+}$, and the charges of these ions, these new peaks were caused by the substitution of F^- on OH^- of $[\text{Al}_{13}]^{2+}$ or $[\text{Al}_{13}]^{3+}$, as given in eqs 2 and 3. According to the species identified from ESI-TOF-MS spectra (Table S3), only Al_3F , Al_3F_2 , Al_3F_3 , and Al_3F_4 were found in filtrates, and no species with more than four F^- ions substituted on Al_{13} were detected in the liquid phase.

Mechanisms of $\text{Al}_{13}^{7+}\text{-F}^-$ Complexation. The $\text{Al}_{13}^{7+}\text{-F}^-$ complexation path was independent of the total Al concentration, which can be confirmed in the following aggregation section. High concentrations (Al_T : 0.3 M, F_T : 0.02 M) were herein chosen for NMR detection. With the introduction of certain amounts of F^- solution, in situ ^{19}F NMR analysis was employed to identify the intermediates during the $\text{Al}_{13}^{7+}\text{-F}^-$ reaction process. The F species in suspension can be also quantified by ^{19}F NMR, and the Gibbs free energy changes ($\Delta_r G$) of the reactions were further calculated to deduce the mechanisms.

According to the ^{19}F NMR spectra gained during the reaction of $\varepsilon\text{-K Al}_{13}^{7+}$ and F^- at different time intervals (Figure 2a inset), no peak near −160 ppm corresponding to unbound F was detected from the beginning of the detection, indicating the extremely fast binding rate. In addition to the NaSiF_6 (external standard) peaks at −129.7 ppm, the peaks of $\mu\text{-F}^a$ (−136.0 ppm), $\mu\text{-F}^b$ (−137.9 ppm), and $\eta\text{-F}$ (−147.9 ppm) are F^- ions replaced on $\mu\text{-OH}^a$, $\mu\text{-OH}^b$, and $\eta\text{-OH}_2$, respectively, and the peaks at −155.9 ppm and −156.5 ppm are assigned to $\text{AlF}_2(\text{H}_2\text{O})_4^+$ and $\text{AlF}(\text{H}_2\text{O})_5^{2+}$.²⁷ According to the quantified results shown in Figure 2a, the concentration of $\eta\text{-F}$ reached the peak value 0.0025 M at reaction time of 4.5 min, which was higher than the concentrations of $\mu\text{-OH}^a$ (0.0017 M) and $\mu\text{-OH}^b$ (0.0008 M). Thus, it was reasonable to conclude that the substitution of F^- on $\eta\text{-OH}_2$ sites was much easier than that on the $\mu\text{-OH}^a/b$ sites. Furthermore, $\Delta_r G$ values, which is used to evaluate the possibility and the spontaneous direction of reaction at constant temperature (T) and pressure (P), for the replacement of $\eta\text{-OH}_2$, $\mu\text{-OH}^a$, and $\mu\text{-OH}^b$ with F^- were calculated (Figure 2b). $\Delta_r G$ for F substitution on $\eta\text{-OH}_2$ (−29.6 kcal mol^{−1}) was much lower than the positive $\Delta_r G$ for F substitution on $\mu\text{-OH}^a$ (6.3 kcal mol^{−1}) and $\mu\text{-OH}^b$ (6.9 kcal mol^{−1}). This indicated the possibility of substitution by F^- on $\eta\text{-OH}_2$ sites, whereas the positive $\Delta_r G$ values hinted the difficulty in direct substitution of F^- on $\mu\text{-OH}^a/b$ sites.

Figure 1. (a) ESI-TOF-MS spectrum of ϵ -K Al_{13} solution. (b–f) Spectra of filtrates from the reaction of ϵ -K Al_{13}^{7+} and F^- : (b) $R_{\text{F:Al}}$ 1:15, (c) $R_{\text{F:Al}}$ 2:15, (d) $R_{\text{F:Al}}$ 3:15, (e) $R_{\text{F:Al}}$ 4:15, (f) $R_{\text{F:Al}}$ 5:15. The cone voltage was 70 V, and Al_T was 0.6 mM.

Figure 2. (a) Concentration changes of fluorinated sites on the ϵ -K Al_{13}^{7+} molecule as a function of time, calculated according to ^{19}F NMR spectra (inset). (b) $\Delta_r G$ values for the reactions of F^- substitution on oxygen sites, and the bond lengths of selected Al–O bonds in ϵ -K Al_{13}^{7+} and $[\text{Al}_{13}\text{F}_6]^{6+}$ (insets).

Figure 3. (a) ESI TOF MS ionic strengths of the filtrates after the reactions of ϵ -K Al_{13}^{7+} and F^- (Al_T : 0.6 mM). (b) Digital image of reaction products of ϵ -K Al_{13}^{7+} and F^- (Al_T : 0.3 M, $R_{F:Al}$: 1:15, 2:15, 3:15, 4:15, 5:15, and 6:15). (c) ^{27}Al NMR spectra and (d) ^{19}F NMR spectra of the liquid phase (Al_T : 0.3 M). (e) Concentrations of Al species in filtrates and the ratio of Al aggregated in precipitates. (f) Concentrations of F species in filtrates and the ratio of F aggregated in precipitates. The Al_T was 0.3 M, and the F_T were 0.02, 0.04, 0.06, 0.08, 0.10, and 0.12 M. Error bars indicate standard deviations, which were calculated according to data of four parallel analyses.

The results were consistent with the replacement abilities at the initial stage of the reaction observed experimentally.

In addition, increased concentrations of $\mu-F^a$ and $\mu-F^b$ were observed at the reaction time from 4.5 to 6.5 min, while the amount of $\eta-F$ decreased. After that, the $\mu-F^b$ further increased, and the concentrations of $\eta-F$ and $\mu-F^a$ decreased with an extended reaction time. However, the total concentration of the three transition species maintained almost the same level at all reaction intervals. The result was due to the transformation of fluoride from $\eta-F$ site to bridging site $\mu-F^{a/b}$, which was previously ascribed to the increased lability of $\mu-OH^{a/b}$ with the introduction of $\eta-F$.²⁸ To revealed the labilities of sites, the bond lengths and bond enthalpies of selected Al–O bonds in ϵ -K Al_{13}^{7+} and $[Al_{13}F^\eta]^{6+}$ were subsequently computed and depicted in Figure 2b. The bond lengths of the Al_O-OH^a were longer than those of the Al_O-OH^b bonds in both ϵ -K Al_{13}^{7+} and $[Al_{13}F^\eta]^{6+}$, which indicated that $\mu-OH^a$ was more liable to be replaced than $\mu-OH^b$. After the replacement of $\eta-OH_2$ with F^- , both the Al_O-OH^a bonds and the Al_O-OH^b bonds around the replacement sites were elongated. Meanwhile, the bond enthalpy of Al_O-OH^a decreased from 42.0 to 29.8 kcal mol⁻¹, the value of which was reduced from 43.0 to 29.7 kcal mol⁻¹ in Al_O-OH^b . The decreased bond enthalpies implied a weakened bond energy between Al and OH, so that the $Al_O-OH^{a/b}$ was readily substituted by F^- in the presence of $\eta-F$.

The substitution by fluoride and the conversion from $\eta-F$ were mainly involved in the fluoride transfer from $\eta-F$ to $\mu-F^{a/b}$. In viewing of the dynamic equilibrium between F^- and $\eta-F$, the substitution of aqueous F^- on $\mu-F^{a/b}$ would be accompanied by the dissociation of $\eta-F$. Thus, the two transformation

paths certainly decreased the $\eta-F$ concentration. Meanwhile, the substitution of F^- on $\mu-OH^a$ synchronously shortened the bond lengths of Al_O-OH^a and Al_O-OH^b and maintained the bond enthalpies of adjacent Al_O-OH^b sites, so that the possibility of the direct conversion from $\mu-F^a$ to $\mu-F^b$ was excluded. Similarly, due to the dynamic equilibrium between $\mu-F^a$ and F^- , the F^- -substitution on $\mu-OH^b$ also resulted in the decrease of $\mu-F^a$.

Aggregation of Fluorinated Al_{13} . In the $Al_{13}^{7+}-F^-$ reaction experiment (Al_T : 0.6 mM), the ionic strengths of filtrates decreased gradually with the increase of $R_{F:Al}$ value (Figure 3a). A coincident phenomenon occurred at a high concentration (Al_T : 0.3 M); the solutions after reaction became visibly turbid with the increase of $R_{F:Al}$ value (Figure 3b). Thus, the reaction of ϵ -K Al_{13}^{7+} and F^- produced particles at both low and high concentrations of Al and F, which has been proved to be controlled by the $R_{F:Al}$ values.

After reaction at 0.3 M Al_T , the species of Al and F in the liquid phases, which were separated from the solids using ultrafiltration membranes (3000 Da), were detected using ^{19}F and ^{27}Al NMR. In addition to the peaks of the external standard ($NaAlO_2$) at 80 ppm, ^{27}Al NMR spectra (Figure 3c) exhibit peaks of ϵ -K Al_{13}^{7+} (63.0 ppm) and Al monomers (Al_m , 0.4–0.9 ppm). ^{19}F NMR spectra (Figure 3d) exhibit peaks of $\mu-F^a$ (–136.0 ppm), $\mu-F^b$ (–137.9 ppm), $\eta-F$ (–147.9 ppm), $AlF_2(H_2O)_4^+$ (–155.9 ppm), and $AlF(H_2O)_5^{2+}$ (–156.5 ppm). According to the NMR spectra, the amounts of Al and F species in the liquid and solid phases were calculated, as depicted in Figure 3e and f. In contrast to the initial percentage content of Al in ϵ -K Al_{13}^{7+} form to Al_T in the prepared Al_{13} solution (98%), the percentage of ϵ -K Al_{13}^{7+} decreased to lower

than 0.1% after reaction at $R_{\text{F:Al}}$ 6:15. With the increase of $R_{\text{F:Al}}$ from 1:15 to 6:15, the amount of generated particles grew, and the proportion of Al and F precipitated in particles increased from 6% to 92% and from 32% to 92%, respectively. F[−]-bound ϵ -K Al_{13}^{7+} in the filtrate decreased from 0.0053 M to undetected (lower than 0.01 mM), while F[−]-bound Al_m in the filtrate increased from 3 mM to 7 mM inversely. Therefore, the majority of F[−] bound and precipitated with ϵ -K Al_{13}^{7+} , and a small amount of dissociation of fluorinated Al_{13} happened at the same time of aggregation and sedimentation.

The molar ratios of Al to F in precipitates were calculated, which equaled the difference between Al_T in the initial reaction solutions and Al_T in the filtrate divided by the difference between F_T in the initial reaction solution and F_T in the filtrate. The molar ratios for 1:15, 2:15, 3:15, 4:15, 5:15, and 6:15 samples were 2.7, 3.0, 3.1, 2.7, 2.5, and 2.5, with standard deviations of 0.17, 0.27, 0.18, 0.11, 0.14, and 0.12, which were calculated according to data of three parallel analyses. As Al_{13} was the main species in filtrates (Figures 1 and 3c), the six characteristic aggregates could be denoted as $\text{Al}_{13}\text{F}_{4.8}$, $\text{Al}_{13}\text{F}_{4.3}$, $\text{Al}_{13}\text{F}_{4.2}$, $\text{Al}_{13}\text{F}_{4.8}$, $\text{Al}_{13}\text{F}_{5.2}$, and $\text{Al}_{13}\text{F}_{5.2}$, which were different with the aqueous species of Al_{13}F_x ($x \leq 4$) obtained via ESI-TOF-MS spectra analyses.

In addition, nearly 32% of F was readily bound and aggregated with ϵ -K Al_{13}^{7+} when the molar ratio of F to Al was 1:15. It was reasonably speculated that the Al_{13}^{7+} structure was liable to be bounded by excessive F[−]. This was in good agreement with the $\Delta_r G$ values for the substitution of F[−] on η -OH₂ depicted in Table 1. A negative Gibbs free energy and enthalpy change was calculated in the F-substitution reaction, the values of which exhibited a positive relationship to the F[−] substitution number. Therefore, the heavy fluorinated Al_{13} should be the thermodynamically preferred form. Furthermore, after introduction of F[−], the increased Gibbs free energy change of reaction between Al_{13}F_n and F[−] implied the difficulty in bonding with more F[−] (Table 1). This result was in good agreement

Table 1. Gibbs Free Energies Changes ($\Delta_r G$) and Enthalpy Changes ($\Delta_r H$) of Each Reaction Forming $[\text{Al}_{13}\text{F}_n]^{(7-n)+}$

reaction products	$\Delta_r G^a$ kcal mol ^{−1}	$\Delta_r H^a$ kcal mol ^{−1}	$\Delta_r G^b$ kcal mol ^{−1}
$[\text{Al}_{13}\text{F}^\eta]^{6+}$	−29.6	−31.0	
$[\text{Al}_{13}\text{F}_2^\eta]^{5+}$	−60.8	−64.4	−31.2
$[\text{Al}_{13}\text{F}_3^\eta]^{4+}$	−87.5	−89.3	−26.7
$[\text{Al}_{13}\text{F}_4^\eta]^{3+}$	−115.1	−118.2	−27.6
$[\text{Al}_{13}\text{F}_5^\eta]^{2+}$	−145.1	−147.7	−30.0
$[\text{Al}_{13}\text{F}_6^\eta]^{+}$	−172.6	−174.8	−27.5
$[\text{Al}_{13}\text{F}_7^\eta]$	−194.2	−193.7	−21.6
$[\text{Al}_{13}\text{F}_8^\eta]^{-}$	−212.5	−207.7	−18.3

^a $\Delta_r G$ and $\Delta_r H$ values of the reactions: $[\text{Al}_{13}]^{7+} + n\text{F}^- = [\text{Al}_{13}\text{F}_n]^{(7-n)+}$.

^b $\Delta_r G$ values of the reactions: $[\text{Al}_{13}\text{F}_n]^{(7-n)+} + \text{F}^- = [\text{Al}_{13}\text{F}_{n+1}]^{(7-n-1)+}$. The Gibbs free energies (G) of the involved species were calculated and listed in Table S4.

with the previous work, which ascribed the difficulty in continuously bonding with more F[−] to the decreased η -OH₂ reactivity and the reduction of positive electrical charge.²⁹

F[−]-substitution on η -OH₂ sites could reduce the net charge of ϵ -K Al_{13}^{7+} from +7 to + (7 − x) (x is the number of η -F sites),^{49,50} which would lowered the repulsive force between fluorinated Al_{13} clusters. The net charge of fluorinated Al_{13}^{7+} after reaction was estimated from the average zeta potential of the solution (Figure 4). As $R_{\text{F:Al}}$ values rose from 1:15 to 6:15,

Figure 4. Zeta potentials of ϵ -K Al_{13} solution after adding NaF (Al_T : 0.6 mM; $R_{\text{F:Al}}$: 1:15, 2:15, 3:15, 4:15, 5:15, and 6:15). The particle size of samples ranged from 1 nm to 8 μm (Figure S3). NaCl was added in each solution to maintain the concentration of 10 mM. The error bars stand for standard deviations, which were recorded from four parallel analyses. The pH, ϵ , η , U/E, count rate, and zeta potential runs of samples were listed in Table S5.

the average zeta potentials of solutions declined from 45.5 to 6.83 mV, which indicated that the balance of the ϵ -K Al_{13} solution was gradually destroyed by F[−], and the clusters in the solutions were increasingly prone to aggregating, especially when $R_{\text{F:Al}}$ was 6:15. Meanwhile, the F[−]-substitution on Al_{13} in solution would be interrupted by the aggregation of fluorinated Al_{13} . Therefore, the reaction of Al_{13} and F were revealed as a complex process, combining F[−]-substitution and fluorinated Al_{13} aggregation synchronously.

Dissociation of Fluorinated Al_{13} . The dissociation of fluorinated ϵ -K Al_{13} (Al_{13}F_x) was validated, since Al_1^+ , Al_3^+ , Al_9^{2+} , and their fluorinated peaks were detected on the ESI-TOF-MS spectrum of the filtrates (Figure 2f, Table S3), which were regarded as the products of the dissociation. Furthermore, the precipitates generated from Al_{13} -F reaction (Al_T : 0.3 M) were detected using MAS NMR measurements. In the ^{27}Al MAS NMR spectra (Figure 5a), strong peaks at 63 ppm were assigned to the central $\text{Al}(\text{O})_4$ tetrahedron of ϵ -K Al_{13} , peaks at 4–5 ppm were assigned to Al_3 , and peaks from 1 to 4 ppm were assigned to Al_2 .^{51–54} The ϵ -K Al_{13} was still the main species in generated precipitates, and a small quantity of oligomers (Al_3 and Al_2) appeared. ^{19}F MAS NMR spectra were fitted using Topspin 3.2 software to acquire the chemical shifts of each fluoride species (Figure 5b–f, Table 2). The precipitates exhibited main peaks of η -F (−144 to −146 ppm), μ -F^a (−129 to −130 ppm), and μ -F^b (−135 to −136 ppm), which represented fluorinated sites on ϵ -K Al_{13} , and minor peaks of fluorinated Al (−152 to −157 ppm). Therefore, it was reasonable to conclude that a small fraction of dissociation took place in the Al_{13} -F complexation and aggregation process. The fluorinated oligomers were the main products from the dissociation, and parts of which dissolved in solution.

The dissociation of fluorinated Al_{13} was mainly relevant to the Al–O bond length. According to the result of previous study, changed Al–O bond lengths, in the presence of fluorine bridges, were liable to destroy the dodecafluorine-substituted Al_{13}^{7+} structure, so that increased the dissociation activity.²⁹ Thus, the bond lengths of Al–O and Al–F in different fluorinated Al_{13} species were further calculated to gain insight into the dissociation (Figure S4). In contrast to the bond lengths of ϵ -K Al_{13}^{7+} , the lengths between the central tetrahedral Al and its bonded oxygens $\mu_4\text{-O}$ ($\text{Al}_t\text{-O}_t$) in $[\text{Al}_{13}\text{F}_5^\eta]^{2+}$ decreased,

Figure 5. MAS NMR spectra of precipitates generated from the reaction of ϵ -K Al_{13}^{7+} and F^- . (a) ^{27}Al MAS NMR spectra. (b–f) ^{19}F MAS NMR spectra with various $R_{\text{F:Al}}$ values: (b) 2:15, (c) 3:15, (d) 4:15, (e) 5:15, (f) 6:15.

Table 2. Experimental MAS NMR Parameters

$R_{\text{F:Al}}$	F sites	$\delta(\text{iso})$ (ppm)	$\delta(\text{CSA})$ (ppm)	$\eta(\text{CSA})$	LB (Hz)	integrated area	overlap
2:15	$\mu\text{-F}^a$	−129.12	−53.02	0.12	3666.23	22.78%	94.85%
	$\mu\text{-F}^b$	−135.93	47.84	0.16	4611.71	31.21%	
	$\eta\text{-F}$	−144.75	−55.05	−0.08	5561.58	46.01%	
3:15	$\mu\text{-F}^a$	−129.03	−40.08	−0.01	3528.56	21.51%	95.70%
	$\mu\text{-F}^b$	−135.26	−60.92	0.29	4824.67	31.61%	
	$\eta\text{-F}$	−145.55	−43.52	0.02	6980.31	46.88%	
4:15	$\mu\text{-F}^a$	−129.02	−39.68	0.26	3125.41	17.95%	95.35%
	$\mu\text{-F}^b$	−135.44	−59.86	0.20	4714.88	35.73%	
	$\eta\text{-F}$	−145.85	−41.05	0.58	6801.49	46.32%	
5:15	$\mu\text{-F}^a$	−129.17	30.7	0.10	3201.74	21.33%	95.70%
	$\mu\text{-F}^b$	−135.25	41.06	0.98	4783.87	33.88%	
	$\eta\text{-F}$	−144.61	−42.20	0.91	6576.35	36.13%	
	Al-F_n	−152.23	−8.89	0.94	6419.17	8.66%	
6:15	$\mu\text{-F}^a$	−129.08	9.48	0.38	3104.65	17.47%	95.62%
	$\mu\text{-F}^b$	−135.63	−52.71	0.20	5292.24	33.91%	
	$\eta\text{-F}$	−145.97	−44.47	0.06	7101.86	37.19%	
	Al-F_n	156.13	3.54	0.89	6320.60	11.43%	

because the substitution of five F atoms on $\eta\text{-OH}_2$ caused the tetrahedral core to contract. Meanwhile, the bonds between octahedral Al and hydroxyl ($\text{Al}_o\text{-OH}^{a/b}$) were elongated due to the substitution of F on $\eta\text{-OH}_2$, as reported in the literature:⁵⁵ substitution by F polarizes the metal–oxygen bond, which results in the weakening and dissociation of $\text{Al-OH}^{a/b}$ bonds. Further, the bond lengths between octahedral Al and the central $\mu_4\text{-O}$ ($\text{Al}_o\text{-O}_t$) became more divergent (Table S6). Consequently, the whole structure became unstable, and the hydroxyl bridges partially dissociated, which allowed the access of water molecules to the central Al.⁵⁶ Moreover, the low net

charge of fluorinated Al_{13} clusters resulted in $\mu_4\text{-O}$ and $\mu_3\text{-O}$ being more easily attacked by H^+ . In summary, the substitution by F prompted the attack of H^+ on $\mu_4\text{-O}$ and the hydration of the central Al, which resulted in the dissociation of fluorinated Al_{13} , releasing a fluorinated trimer and fluorinated nonamer; the fluorinated nonamer further dissociated into trimers, and subsequently fluorinated trimers broke into monomers via protonation of the central $\mu_3\text{-O}$ group and hydration of Al (Figure 6).

Overall, the fate of $\text{Al}_{13}\text{-F}$ induced by F^- substitution provided an ideal platform for the removal of F^- using a coagulation approach. The amount of soluble Al in the form of

Figure 6. Dissociation diagram of fluorinated Al_{13} .

Al-F complexes, especially in some natural waters, might bring about much difficulties in the F^- removal. Therefore, it is reasonable to increase Al_{13} ratio, as it is beneficial to Al-F coagulation process. Meanwhile, excess F^- substitution might induce the dissociation of Al_{13} , and this discovery will help optimize the dosage of Al in the coagulation process.

Environmental Significance. For the fluoride contamination in drinking water, coagulation or adsorption by $\epsilon\text{-K Al}_{13}^{7+}$ polymer has been taken as an effective path for fluoride removal. Complexation, neutralization, aggregation, precipitation, and dissociation of $\epsilon\text{-K Al}_{13}^{7+}$ polymer coexisting with F^- were herein examined and discussed in detail, which will provide a valuable basis for the application and regulation of $\epsilon\text{-K Al}_{13}^{7+}$ for the high-efficient fluoride removal. The fluorinated Al_{13} aggregation behavior indicated that $R_{\text{Al:F}}$ of 15:6 should be an optimal value for $\text{Al}_{13}\text{-F}$ complexation. In addition to complexation, adsorption and sweep by the aluminum flocs also play a crucial role for fluoride removal in coagulation process, where the $R_{\text{Al:F}}$ ratio was usually lower than 15:6 in the practical water treatment process. The findings will provide better insight into the coagulation process, guiding the dosage of Al salt, thereby ultimately enhancing the F^- removal process in practical water treatment process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05876.

Additional experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

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