Effect of pH on the aluminum salts hydrolysis during coagulation process: Formation and decomposition of polymeric aluminum species

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ABSTRACT

Effect of pH on the aluminum chloride hydrolysis at low concentration was investigated in detail by electrospray ionization (ESI) mass spectrometry. In particular, formation and decomposition processes of polymeric aluminum species were discussed. When coagulant AlCl_3 was diluted to normal coagulant dose (1.5×10^{-4} mol/L), hydrolysis occurred immediately. Monomeric and dimeric aluminum species were the main products at pH 4.0. With pH increasing, hydrolysis and polymerization processes were accelerated. Monomeric and dimeric aluminum species hydrolyzed and polymerized into small polymeric aluminum species (Al_3 – Al_5 species) at pH 4.8. Through aggregation and self-assembly, the small polymeric aluminum species polymerized into median polymeric species (Al_6 – Al_{10} species) at pH 5.0. In the same way, small and median polymeric aluminum species further aggregated into large polymeric species (Al_{11} – Al_{21} species). When pH was up to 5.8, metastable median and large polymers species decomposed into small aluminum species, then further disaggregated into dimeric species. With pH increased to 6.4, majority of aluminum species formed to $\text{Al}(\text{OH})_3$ amorphous flocs. Accordingly, coagulant hydrolysis mechanism from polymerization toward decomposition was proposed. Furthermore, formation and decomposition of polymeric aluminum species in AlCl_3 solution followed the “Core-links” model, while those of Keggin- Al_{13} species in polyaluminum solution was based on the “Cage-like” model.

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1. Introduction

Aluminum salts and aluminum species of coagulants have been attracting many attentions over the past 100 years [1–3]. Many analytical methods have been used to characterize and quantify aluminum species. Traditional methods include potentiometric titration [4], Al–ferron timed spectrophotometric assay [5,6] and ^{27}Al NMR spectroscopy [7,8]. In addition, X-ray diffraction [9] and Raman spectroscopy [10] are used as aluminum speciation analysis. Al–ferron assay and ^{27}Al NMR spectroscopy were common means to identify aluminum speciation of coagulant. ^{27}Al NMR spectroscopy offers information about monomeric, dimeric aluminum species and highly symmetric Keggin- Al_{13} (K-Al_{13} , $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$) species [11]. However, investigations on speciation of aluminum salts at low concentrations in nature and coagulation are hampered by the detection limits of ^{27}Al NMR. The speciation obtained by Al–ferron method is only a rough classification based on kinetic measurements. Thus, to accurately identify aluminum coagulant of structure characterization and quantify aluminum species during hydrolysis is too difficult.

Recently, Sarpola [12] applied a well established method to aluminum complexes using electrospray ionization (ESI) mass spectrometry in his PhD thesis. Using ESI method, Sarpola et al. [13,14] identified hydrolysis products of AlCl_3 . Furthermore, aluminum salts in the presence of sulfate were emphasized investigated [15]. In contrast to AlCl_3 , Rămö et al. [16] demonstrated that aluminum speciation variation of highly 80% and moderately 42% basic polyaluminum chloride (PACl) at different pH values using ESI-MS. Therefore, based on detecting mass to charge ratio (m/z) of complexes, the ESI-MS measurement has been proved as a good method for aluminum speciation.

Scientists have done much research focuses on the aluminum salts hydrolysis and their hydrolysis products [1,2,17]. In various studies, pH was believed to be one of the most important factors that affect the aluminum species present in the aqueous solution [6,18–21]. Based on the results from X-ray and light-scattering tests, Hayden and Rubin [18] calculated the effect of the pH on aluminum hydrolysis behavior. Subsequently, Bottero et al. [19] did a similar study of the pH effect with the use of the NMR technique. In their results, K-Al_{13} species formed in weak acidic condition. Similarly, Arnson [20] reported the existence of polymeric Al_8 species in weak acidic pH range. However, there is still no agreement on the aluminum hydrolysis–polymerization mecha-

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Table 1
Characteristics of coagulant by ^{27}Al NMR and ferron assay.

Coagulant	Al_T (mol/L)	pH	Al speciation (%) ^a					
			Al_m	K- Al_{13}	Al_un	Al_a	Al_b	Al_c
AlCl_3	0.55	2.21	100	0	0	96.2	3.8	0

^a Al_m : monomers and dimers; Al_un : $\text{Al}_\text{T} - [\text{Al}_\text{m} + \text{K-}\text{Al}_{13}]$; the reaction time of Al_a and ferron reagent was 1 min, and the aluminum species reacting with the ferron reagent before 120 min represented $[\text{Al}_\text{a} + \text{Al}_\text{b}]$; Al_c : $\text{Al}_\text{T} - [\text{Al}_\text{a} + \text{Al}_\text{b}]$.

nism. Furthermore, the effect of pH on the formation of polymeric species still needs further investigation, especially for traditional aluminum salts hydrolysis at low concentration.

The primary objective of the present research was to determine hydrolysis polymerization mechanism of traditional aluminum salts. Effect of pH on the AlCl_3 hydrolysis at low concentration (1.5×10^{-4} mol/L) was studied in detail by ESI mass spectrometry. Particular emphasis was paid to formation and decomposition processes of polymeric aluminum species.

2. Materials and methods

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Guaranteed Reagent, Beijing Chemical Regents Company) was used in this study. Total aluminum concentrations (Al_T) were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 2000, Perkin Elmer, UK). Initial aluminum speciation of coagulant was characterized by ^{27}Al NMR and ferron colorimetric method. Details of the operating approaches and parameters of the apparatus can be found in the literature [22]. The original aluminum speciation characteristic of the coagulant used was summarized in Table 1.

To investigate aluminum hydrolysis of the coagulant at different pH values, the coagulant was diluted to a concentration of 1.5×10^{-4} mol/L. In our experiments, “fresh” solutions were used mostly in order to be consistent with the condition of coagulation process. The pH values of fresh solutions were adjusted after diluted. Aged solutions were first diluted, then pH was adjusted after an aging time. Tetramethylammonium hydroxide pentahydrate, $(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}$ (TMA, Analytical Reagent, Beijing Chemical Regents Company) or HCl solution was added into the solution to control pH. All pH measurements (± 0.03) were performed with a pH meter (720A, Thermo Orion, USA) equipped with an electrode. The electrode was calibrated using standard buffers (pH 4.01 and pH 7.00). After 3-min mixing, the solutions were injected into the mass spectrometer. Deionized water was used to provide baseline species distributions data.

The ESI TOF mass spectra were recorded with a micromass hybrid quadrupole time of flight mass spectrometer (2695XE Micro, Waters, USA) equipped with an electrospray ion source. All ESI mass spectral data were performed in positive ion mode. The solutions were introduced into the spectrometer at a flow-rate of 10 $\mu\text{L}/\text{min}$. The instrumental conditions were as follows: capillary voltage 3500.0 V, sample cone voltage 70 V (40 and 150 V), Ff lens 200 V, extraction cone voltage 5 V, source temperature 120 $^\circ\text{C}$, cone gas (N_2) flow rate 300 L/h, mass range 80–1000. The major ions in the ESI-MS spectra, which represented specific aluminum complexes, were selected for the ESI-MS/MS study.

3. Results and discussion

3.1. Effect of pH on the aluminum salts hydrolysis

Initial aluminum concentration of the coagulant was high (0.55 mol/L) and hydrolysis of aluminum salts were very slow. (Details and ^{27}Al NMR spectrum of initial AlCl_3 solution are presented in Supporting material.) After diluted to a concentration of

1.5×10^{-4} mol/L (normal dose of coagulation), aluminum speciation of the coagulant made a change.

The ESI-MS spectrum of the AlCl_3 solution (1.5×10^{-4} mol/L) at pH 4.0 is shown in Fig. 1a. The most intense peaks were assigned to the monomers $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_{2-3}]^+$ at mass to charge ratio (m/z) 97 (100%) and m/z 115 with 81% relative intensity. Dimeric aluminum species $[\text{Al}_2\text{O}_2(\text{OH})(\text{H}_2\text{O})_{0-5}]^+$ at m/z 103, 121, 139, 157, 175 and 193 were also the dominating species. In addition, the series of polymers containing Al_3 cores (at m/z 145, 163, 181, 199, 217, 235 and 253) and Al_5 cores (m/z 124, 142, 160 and 178) were observed as well in the spectra at pH 4.0.

When pH was raised to 4.8 (Fig. 1b), aluminum speciation distribution changed a lot from that at pH 4.0. With the concentration of OH/Al increased, aluminum salts further hydrolyzed and peaks moved to a higher m/z range. Monomers were diminished to less, whereas dimers $[\text{Al}_2\text{O}_2(\text{OH})(\text{H}_2\text{O})_{0-3}]^+$ at m/z 103 (42%), 121 (100%), 139 (38%) and 157 (18%) dominated in the spectra. Trimers $[\text{Al}_3\text{O}_4(\text{H}_2\text{O})_{0-5}]^+$ at m/z 145, 163, 181, 199, 217 and 235 increased to be the major species as well. Additionally, intense peaks at m/z 277 and 247 began to appear. The series of small polymers containing Al_4 and Al_5 cores were observed. Multi-charged polymeric series containing Al_8 or Al_{11} , Al_{12} , Al_{13} cores were also observed in the spectra at pH 4.8.

The ESI-MS spectrum of the AlCl_3 solution at pH 5.0 (Fig. 1c), peaks at m/z 277 (100%) and 247 (73%) became the dominating species in the spectrum. Dimeric series decreased but still were the major species. Polymeric aluminum species at m/z 328, 337, 213, 298 and 307, which began to appear at pH 4.8, all increased at pH 5.0. In addition, the series of polymers containing Al_4 and Al_5 cores were observed. Median and large polymeric aluminum species containing Al_{10} , Al_{11} and Al_{14} cores were observed as well in the spectra at pH 5.0.

When pH was raised to 5.2 (Fig. 1d), aluminum salts further hydrolyzed and aluminum speciation distribution was much different from initial aluminum speciation of the coagulant. The ions at m/z 337 (100%) and 328 (56%) became to dominate in the spectrum. This is consistent with our previous observations [23]. The signal at m/z 328 was assigned to $[\text{Al}_{13}\text{O}_{18}(\text{OH})]^{2+}$, while the signal at m/z 337 was assigned to $[\text{Al}_{13}\text{O}_{17}(\text{OH})_3]^{2+}$. Dimeric series at m/z 103, 121, 139 also were the major species. Additionally, the series of polymers containing Al_3 , Al_4 , Al_7 , Al_{14} , Al_{15} and Al_{21} cores were observed as well in the spectra at pH 5.2.

At pH 5.8, though aluminum salts further hydrolyzed, total ions began to decrease. As shown in Fig. 1e, aluminum species at pH 5.8 decreased a lot from that at pH 5.2. Al_{13} species at m/z 337 and 328 were diminished, whereas dimeric at m/z 103, 121, and 157 dominated in the spectrum. In addition, trimeric aluminum species and tetrameric aluminum species were also observed in the spectrum. The series of polymers containing Al_7 , Al_{14} , Al_{16} cores were observed as well in the spectra at pH 5.8.

As shown in Fig. 1f, when pH was raised to 6.4, amorphous flocs of $\text{Al}(\text{OH})_3$ formed and total ions largely decreased. Dimeric species diminished to less, but still were the dominating species in the spectrum. In addition, trimeric and tetrameric aluminum species were observed in the spectrum. The series of polymers containing Al_7 and Al_{13} – Al_{16} cores were observed as well in the spectra at pH 6.4.

A very intense $[\text{TMA}_2\text{Cl}]^+$ adduct signal at m/z 183 was observed at both pH 5.2, 5.8 and 6.4. According to the previous study [12,23], the presence of TMA adducts was also observed in the samples due to adjusting of pH by TMA. In addition, series of signals at m/z 245, 261, 319 and 335 were assigned to $[\text{K}_3\text{NaCl}_3]^+$, $[\text{K}_4\text{Cl}_3]^+$, $[\text{K}_4\text{NaCl}_4]^+$ and $[\text{K}_5\text{Cl}_4]^+$, respectively. Potassium is an impurity that may originate from aluminum solutions.

In this study, both lower (40 V) and higher sample cone voltages (150 V) had effect on the aluminum speciation. On one hand,

Fig. 1. ESI-MS spectrum of AlCl_3 (1.5×10^{-4} mol/L): (a) pH 4.0; (b) pH 4.8; (c) pH 5.0; (d) pH 5.2; (e) pH 5.8; (f) pH 6.4.

similar spectra were observed at lower sample cone voltage (40 V), but signal intensity was low as well. On the other hand, at higher sample cone voltage (150 V), aluminum species were simplified. Aluminum species with water series did not appear, but majority in the form of single ion (e.g. $[\text{Al}_5\text{O}_7]^+$, $[\text{Al}_7\text{O}_{10}]^+$, $[\text{Al}_{11}\text{O}_{16}]^+$ and $[\text{Al}_{13}\text{O}_{19}]^+$).

3.2. Identification and fragmentation of hydrolyzed aluminum species

In results of Sarpola et al. [12], most of small aluminum complexes (10×10^{-3} and 100×10^{-3} mol/L) contained not only hydroxo and oxo but also chloro ligands. In our work, few aluminum complexes with chloro ligands appeared at a lower concentration. The major ions in the spectra, which represented specific aluminum complexes, were selected for further identification by ESI-MS/MS product ion scan.

The fragments and proposed reactions of ions at m/z 163, 277 and 247 are displayed in Table 2. The signals were assigned to $[\text{Al}_3\text{O}_4(\text{H}_2\text{O})]^+$, $[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]^+$ and $[\text{Al}_5\text{O}_7]^+$, respectively. Gaussian water series dominated in the fragment ion spectra. It was proposed earlier that aluminum complexes could capture aqua ligands in the collision chamber, and the reactions between aluminum complexes and water molecules were extremely rapid [14]. In MS/MS spectra, $[\text{Al}_3\text{O}_4(\text{H}_2\text{O})]^+$ may lose aluminum to produce dimeric ions (m/z 103 and 121). This is consistent with previous work reported by Sarpola et al. [14], except with a higher collision energy (35 eV). Similarly, parent ion $[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]^+$ may lose aluminum to produce trimeric species $[\text{Al}_3\text{O}_4(\text{H}_2\text{O})_{4-5}]^+$ (at m/z 217 and 235). Additionally, through changing two hydroxo groups to a oxo group, two parent ions $[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]^+$ could combine together, and produced daughter ions at m/z 232 and 268. Moreover, one (three) aluminum(s) may be removed from

Table 2Fragments and proposed fragmentation reactions of the ions at m/z 163, 277 and 247 (AlCl_3 , 1.5×10^{-4} mol/L).

m/z	Species	m/z 163 ^a	m/z 277 ^a	m/z 247 ^{a,b}
103	$[\text{Al}_2\text{O}_2(\text{OH})]^+$	$-\text{AlO}(\text{OH})$		
121	$[\text{Al}_2\text{O}_2(\text{OH})(\text{H}_2\text{O})]^+$	$-\text{AlO}(\text{OH}) + \text{H}_2\text{O}$		
145	$[\text{Al}_3\text{O}_4]^+$	$-\text{H}_2\text{O}$		
163	$[\text{Al}_3\text{O}_4(\text{H}_2\text{O})]^+$	Parent		
175 ^{b,c}	$[\text{Al}_7\text{O}_9(\text{OH})]^{2+}$			$-\text{Al}_3\text{O}_4(\text{OH}) + \text{H}_2\text{O}$
181	$[\text{Al}_3\text{O}_4(\text{H}_2\text{O})_2]^+$	$+\text{H}_2\text{O}$		
184 ^{a,b,c}	$[\text{Al}_7\text{O}_9(\text{OH})(\text{H}_2\text{O})]^{2+}$			$-\text{Al}_3\text{O}_4(\text{OH}) + 2\text{H}_2\text{O}$
193 ^{b,c}	$[\text{Al}_7\text{O}_9(\text{OH})(\text{H}_2\text{O})_2]^{2+}$			$-\text{Al}_3\text{O}_4(\text{OH}) + 3\text{H}_2\text{O}$
199	$[\text{Al}_3\text{O}_4(\text{H}_2\text{O})_3]^+$	$+2\text{H}_2\text{O}$		
202 ^{a,b,c}	$[\text{Al}_7\text{O}_9(\text{OH})(\text{H}_2\text{O})_3]^{2+}$			$-\text{Al}_3\text{O}_4(\text{OH}) + 4\text{H}_2\text{O}$
217	$[\text{Al}_3\text{O}_4(\text{H}_2\text{O})_4]^+$	$+3\text{H}_2\text{O}$	$-\text{AlO}(\text{OH})$	
223	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})]^+$		$-3\text{H}_2\text{O}$	
232 ^c	$[\text{Al}_8\text{O}_{11}(\text{H}_2\text{O})_4]^{2+}$		$-5\text{H}_2\text{O}$	
235	$[\text{Al}_3\text{O}_4(\text{H}_2\text{O})_5]^+$		$-\text{AlO}(\text{OH}) + \text{H}_2\text{O}$	
241	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_2]^+$		$-2\text{H}_2\text{O}$	
247	$[\text{Al}_5\text{O}_7]^+$		$-\text{Al}_3\text{O}_4]^+ - 9\text{H}_2\text{O}^c$	Parent
	$[\text{Al}_{10}\text{O}_{14}]^{2+}$ ^c			
259	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_3]^+$		$-\text{H}_2\text{O}$	
268 ^c	$[\text{Al}_8\text{O}_{11}(\text{H}_2\text{O})_8]^{2+}$		$-\text{H}_2\text{O}$	
277	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]^+$		Parent	
295	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_5]^+$		$+\text{H}_2\text{O}$	
313	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_6]^+$		$+2\text{H}_2\text{O}$	
349 ^c	$[\text{Al}_7\text{O}_{10}]^+$		$-\text{AlO}]^+ - 9\text{H}_2\text{O}$	$-\text{Al}_3\text{O}_4]^+ \text{ }^{a,b}$
451 ^{a,b,c}	$[\text{Al}_9\text{O}_{13}]^+$			$-\text{AlO}]^+$
655 ^{b,d}	$[\text{Al}_{13}\text{O}_{19}]^+$			$-2[\text{AlO}]^+$

^a Sample cone voltage 70 V, collision energy 20 eV.^b Sample cone voltage 70 V, collision energy 30 eV.^c Two parent ions combined together in reactions.^d Three parent ions combined together in reactions.

the cores when two $[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]^+$ combined together, then ion at m/z 349 (247) was produced. Different from trimers and tetramers, parent ion $[\text{Al}_5\text{O}_7]^+$ was easier to aggregate by self-assembly to form $[\text{Al}_{10}\text{O}_{14}]^{2+}$. Hence, parent ion $[\text{Al}_5\text{O}_7]^+$ had characteristics of Al_{10} species. One (three) aluminum molecule(s) could be removed from the cores when two Al_5 combined together. This is consistent with our previous study [23] that the Al_{10} species may be metastable and transient, and thus Al_{10} core can break easily. When three $[\text{Al}_5\text{O}_7]^+$ ions combined together, two aluminum molecules could be removed from the cores.

The fragments and proposed reactions of ions at m/z 213, 219, 298 and 349 are shown in Table 3. The signals at m/z 213, 219 and 298 were assigned to $[\text{Al}_{13}\text{O}_{18}(\text{H}_2\text{O})_{0-1}]^{3+}$ and $[\text{Al}_{12}\text{O}_{17}]^{2+}$, respectively. Parent ions at both m/z 213 and 219 were found to produce a prominent product ion peak at m/z 298. One aluminum molecule (and one water) could be removed from the $[\text{Al}_{13}\text{O}_{18}(\text{H}_2\text{O})_{0-1}]^{3+}$ to form $[\text{Al}_{12}\text{O}_{17}]^{2+}$, while the Al_{13} structure also could be rid of three or five aluminum molecules. It is different from Sarpola et al. [12] reported that Al_{13} core was highly stable, and to break its structure required very high collision energies (75 eV). The reason may be that the new formed Al_{13} species in this study were not stable as aged Al_{13} structures. Additionally, $[\text{Al}_{12}\text{O}_{17}]^{2+}$ could break up into Al_4 species and Al_8 species. When two $[\text{Al}_{12}\text{O}_{17}]^{2+}$ ions combined together, five (seven) aluminum molecules could be removed. Parent ions at m/z 349 were assigned to $[\text{Al}_{14}\text{O}_{20}]^{2+}$ (overlapping signal $[\text{Al}_{11}\text{O}_{11}(\text{OH})_9(\text{H}_2\text{O})_4]^{2+}$). On one hand, similar to Al_5 species, $[\text{Al}_7\text{O}_{10}]^+$ was easier to aggregate by self-assembly to form $[\text{Al}_{14}\text{O}_{20}]^{2+}$. Hence, the parent ions at m/z 349 had the same characteristics as Al_{14} species at m/z 358. $[\text{Al}_{14}\text{O}_{20}]^{2+}$ species could break up into Al_5 and Al_9 (or Al_4 and Al_{10}) ions. Additionally, one (two) aluminum molecule could be removed from the Al_{14} cores. When three $[\text{Al}_7\text{O}_{10}]^+$ ions at m/z 367 combined together, one aluminum molecules may be removed from the cores. On the other hand, parent ion $[\text{Al}_{11}\text{O}_{11}(\text{OH})_9(\text{H}_2\text{O})_4]^{2+}$ lost or added water molecule(s) to produce series of daughter ions at m/z 313, 331 and 367. At higher sample cone voltage (150 V), aluminum species were simplified. In

the spectra at 150 V, signal at m/z 349 did not exhibit the characteristic of Al_{14} species. Thus, m/z 349 was assigned to $[\text{Al}_7\text{O}_{10}]^+$. Therefore, at higher sample cone voltage, reactions that aluminum complexes self-aggregated and captured aqua ligands in the collision chamber may be restrained.

According to the MS/MS results discussed above and supplemented in Supporting material, majority of signals appeared in the ESI-MS spectra were assigned to corresponding aluminum species. These aluminum species, peaks and their relative intensities are summarized in Table 4.

3.3. Formation and decomposition of polymeric aluminum species

The abundance of polymeric aluminum species was evaluated semi-quantitatively by the signal intensities of relative to aluminum species [12,16]. Five aluminum species were classified as follows: Al_1 – Al_2 species (monomeric and dimeric aluminum complexes), Al_3 – Al_5 species (small polymeric aluminum species), Al_6 – Al_{10} species (median polymeric species), Al_{11} – Al_{21} species (large polymeric species) and undetected part (Al_u , i.e., solid-phase $\text{Al}(\text{OH})_3$ and/or $\text{Al}(\text{OH})_4^-$). Summing the signal intensities of all aluminum species at pH 4.0 expressed them as total aluminum ion counts (Al_t). The difference between Al_t and $[\text{Al}_1\text{–Al}_2 + \text{Al}_3\text{–Al}_5 + \text{Al}_6\text{–Al}_{10} + \text{Al}_{11}\text{–Al}_{21}]$ was Al_u .

The distribution of aluminum species (normal dose) as a function of pH value are illustrated in Fig. 2. The monomeric and dimeric aluminum complexes decreased rapidly with the increase of pH and reached minimum at pH 5.0. That is due to hydrolysis to form polymeric species. However, polymeric species were not stable. One (or two) aluminum molecule(s) can be removed from polymers to form new species. This compares favorably with the above MS/MS results. Thus, the Al_1 – Al_2 species increased slightly in pH region of 5.2–5.8. In contrast, small polymeric species (Al_3 – Al_5 species) increased and reached maximum at pH 4.8. That may be attributed to that monomers and dimers polymerized into small polymeric species. In this study, polymeric aluminum species need collision energies (20–30 eV) or external conditions (e.g. pH vari-

Table 3Fragments and proposed fragmentation reactions of the ions at m/z 213, 219, 298 and 349 (AlCl_3 , 1.5×10^{-4} mol/L).

m/z	Species	m/z 213 ^a	m/z 219 ^a	m/z 298 ^a	m/z 349 ^a
165	$[\text{Al}_{10}\text{O}_{13}(\text{OH})]^{3+}$		$-\text{Al}_3\text{O}_4(\text{OH})$		
183	$[\text{Al}_{10}\text{O}_{13}(\text{OH})(\text{H}_2\text{O})_3]^{3+}$		$-\text{Al}_3\text{O}_4(\text{OH}) + 3\text{H}_2\text{O}$		
196	$[\text{Al}_8\text{O}_{11}]^{2+}$	$-\text{Al}_5\text{O}_7]^+$			
201	$[\text{Al}_{10}\text{O}_{13}(\text{OH})(\text{H}_2\text{O})_6]^{3+}$		$-\text{Al}_3\text{O}_4(\text{OH}) + 6\text{H}_2\text{O}$		
213	$[\text{Al}_{13}\text{O}_{18}]^{3+}$	Parent	$-\text{H}_2\text{O}$		
219	$[\text{Al}_{13}\text{O}_{17}(\text{OH})_2]^{3+}$		Parent		
241	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_2]^+$			$-\text{Al}_8\text{O}_{11}(\text{OH})]^+ + 3\text{H}_2\text{O}$	
247	$[\text{Al}_5\text{O}_7]^+$	$-\text{Al}_8\text{O}_{11}]^{2+}$			
253	$[\text{Al}_9\text{O}_{12}(\text{OH})(\text{H}_2\text{O})_3]^{2+}$				$-\text{Al}_5\text{O}_7(\text{OH}) + 4\text{H}_2\text{O}$
259	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_3]^+$			$-\text{Al}_8\text{O}_{11}(\text{OH})]^+ + 4\text{H}_2\text{O}$	
274	$[\text{Al}_{10}\text{O}_{14}(\text{H}_2\text{O})_3]^{2+}$				$-\text{Al}_4\text{O}_6 + 3\text{H}_2\text{O}$
277	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4]^+$			$-\text{Al}_8\text{O}_{11}(\text{OH})]^+ + 5\text{H}_2\text{O}$	
281 ^d	$[\text{Al}_{17}\text{O}_{24}]^{3+}$			$-\text{Al}_7\text{O}_{10}]^+$	
295	$[\text{Al}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_5]^+$			$-\text{Al}_8\text{O}_{11}(\text{OH})]^+ + 6\text{H}_2\text{O}$	$-\text{Al}_{10}\text{O}_{14}(\text{OH})]^+ + 6\text{H}_2\text{O}$
298	$[\text{Al}_{12}\text{O}_{17}]^{2+}$	$-\text{AlO}]^+$	$-\text{AlO}]^+ - \text{H}_2\text{O}$	Parent	$-\text{Al}_2\text{O}_3$
313 ^c	$[\text{Al}_{11}\text{O}_{11}(\text{OH})_9]^{2+}$				$-4\text{H}_2\text{O}$
315 ^d	$[\text{Al}_{19}\text{O}_{27}]^{3+}$			$-\text{Al}_5\text{O}_7]^+$	
328	$[\text{Al}_{13}\text{O}_{18}(\text{OH})]^{2+}$				$-\text{AlO}(\text{OH}) + \text{H}_2\text{O}$
331 ^c	$[\text{Al}_{11}\text{O}_{11}(\text{OH})_9(\text{H}_2\text{O})_2]^{2+}$				$-2\text{H}_2\text{O}$
349	$[\text{Al}_{14}\text{O}_{20}]^{2+}$				Parent
	$[\text{Al}_{17}\text{O}_{10}]^+{}^b$				
	$[\text{Al}_{11}\text{O}_{11}(\text{OH})_9(\text{H}_2\text{O})_4]^{2+}{}^c$				
367	$[\text{Al}_7\text{O}_9(\text{OH})_2]^+{}^b$				$+\text{H}_2\text{O}$
	$[\text{Al}_{11}\text{O}_{11}(\text{OH})_9(\text{H}_2\text{O})_6]^{2+}{}^c$				
385 ^b	$[\text{Al}_7\text{O}_8(\text{OH})_4]^+$				$+2\text{H}_2\text{O}$
502 ^{b,e}	$[\text{Al}_{20}\text{O}_{29}]^{2+}$				$-\text{AlO}^+$
655 ^{b,d}	$[\text{Al}_{13}\text{O}_{19}]^+$				$-\text{AlO}^+$

^a Sample cone voltage 70 V, collision energy 20 eV.^b Sample cone voltage 150 V, collision energy 20 eV.^c Overlapped parent ion $[\text{Al}_{11}\text{O}_{11}(\text{OH})_9(\text{H}_2\text{O})_4]^{2+}$ and its products.^d Two parent ions combined together in reactions.^e Three parent ions combined together in reactions.

ation) to decompose. The lower bond energy, the lower collision energy is needed to break (or form) structure. Thus, no matter formation or decomposition of polymers, the lowest energy state preferentially occurred. According to the MS/MS results discussed above, Al_3 (Al_4 or Al_5) species can lose aluminum to produce dimeric (trimeric or tetrameric) ions with a low collision energy (20 eV). Similarly, polymerization of aluminum species followed the same way as decomposition of those with the lowest energies. That is, monomeric and dimeric aluminum species could hydrolyzed and polymerized into Al_3 species, and then further polymerized into Al_4 and Al_5 species. However, the Al_3 – Al_5 species decreased at pH 5.0–5.2. This is consistent with the MS/MS results. Two trimers (tetramers) could combine together to form new species. Al_5 species were easier to aggregate by self-assembly as well. When pH was further raised, these species did not change a lot. Similar trends were observable for large polymeric species. A rapid increase of the Al_{11} – Al_{21} species was observed in the region of pH 4.0–5.0. The maximum of these species occurred at pH 5.0–5.2. In the same way, polymerization of Al_{11} – Al_{21} species was consistent with the MS/MS results of decomposition. For instance, $\text{Al}_{12}\text{O}_{17}$ broke up into Al_4 (Al_5) species and Al_8 (Al_7) species with a collision energy of 20 eV. Correspondingly, small and median polymeric aluminum species could aggregate into large polymeric species. However, large polymers, which were not stable, could decompose into medium and small aluminum species. Thus, a rapid decrease of the Al_{11} – Al_{21} species occurred at pH 5.2–6.4. Additionally, the distribution of the Al_6 – Al_{10} species was similar to that of the Al_{11} – Al_{21} species but at a reduced scale. When small aluminum species combined together, the Al_6 – Al_{10} species formed. However, these medium aluminum species, which were transient species, further polymerized into large species. Furthermore, the content of Al_u was increasing throughout the pH range investigated. In this study, Al_u species mainly included $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$. With the pH increasing, finally product of the polymer-

Fig. 2. Distribution of aluminum species as a function of pH value for AlCl_3 (1.5×10^{-4} mol/L).

ization and decomposition was $\text{Al}(\text{OH})_3$. Additionally, aging time significantly influenced polymerization. In aged (8–12 hours) solutions, the total ion count (TIC) diminished to less at pH 4.74. That is, formation of $\text{Al}(\text{OH})_3$ amorphous flocs at a lower pH range. In addition, polymeric aluminum species formed in the aged solutions were more stable than new formed ones.

On the basis of our ESI results, the coagulant AlCl_3 hydrolysis with increased OH/Al was demonstrated as a process of polymeric aluminum species formation and decomposition. As shown in Scheme 1, when initial AlCl_3 with a 0.5 mol/L concentration was diluted to 1.5×10^{-4} mol/L, hydrolysis occurred immediately. At the beginning, monomeric and dimeric aluminum species were the main products (Fig. 1a). With pH rising, the ratio of OH/Al was increase, thus hydrolysis and polymerization processes were accelerated. Monomeric and dimeric aluminum species hydrolyzed and

Table 4Distribution of signals in the ESI-MS spectra and corresponding aluminum species at different pH conditions (AlCl_3 , 1.5×10^{-4} mol/L, pH 4.0–6.4).

Aluminum species	Signals (m/z) and relative intensities (%)					
	pH 4.0	pH 4.8	pH 5.0	pH 5.2	pH 5.8	pH 6.4
Al ₁	m/z 97: 100% m/z 115: 44%			m/z 97: 13% m/z 115: 31%	m/z 97: 17%	m/z 97: 11%
Al ₂	m/z 103: 7% m/z 121: 20% m/z 139: 31% m/z 157: 66% m/z 175: 58% m/z 193: 15%	m/z 103: 42% m/z 121: 100% m/z 139: 38% m/z 157: 18%	m/z 103: 33% m/z 121: 75% m/z 139: 27% m/z 157: 16%	m/z 103: 55% m/z 121: 83% m/z 139: 28% m/z 157: 17%	m/z 103: 56% m/z 121: 100% m/z 139: 11% m/z 157: 16%	m/z 103: 40% m/z 121: 67% m/z 139: 10% m/z 157: 12%
Al ₃	m/z 145: 3% m/z 163: 7% m/z 181: 14% m/z 199: 15% m/z 235: 13% m/z 253: 10%	m/z 145: 10% m/z 163: 38% m/z 181: 43% m/z 199: 30% m/z 217: 16% m/z 235: 12%	m/z 145: 10% m/z 163: 35% m/z 181: 36% m/z 199: 23% m/z 217: 7% m/z 235: 7%	m/z 91: 7% m/z 235: 16%	m/z 91: 12%	m/z 91: 7%
Al ₄		m/z 205: 10% m/z 223: 10% m/z 241: 15% m/z 259: 10% m/z 277: 44% m/z 295: 7%	m/z 93: 9% m/z 205: 11% m/z 223: 7% m/z 241: 10% m/z 277: 100% m/z 295: 6%	m/z 81: 4% m/z 87: 27% m/z 99: 16% m/z 105: 66% m/z 313: 8%	m/z 81: 6% m/z 87: 29% m/z 99: 14% m/z 105: 66%	m/z 81: 3% m/z 87: 20% m/z 93: 3% m/z 99: 8% m/z 105: 37% m/z 123: 20% m/z 147: 12%
Al ₅	m/z 124: 7% m/z 142: 15% m/z 160: 21%	m/z 247: 40% m/z 265: 5% m/z 283: 5% m/z 301: 9% m/z 319: 6% m/z 349: 9%	m/z 247: 73% m/z 301: 9%	m/z 319: 8%		
Al ₇				m/z 117: 23% m/z 123: 31% m/z 135: 21% m/z 147: 15% m/z 367: 11% m/z 385: 9%	m/z 117: 27% m/z 123: 31% m/z 135: 24% m/z 147: 15% m/z 202: 7% m/z 349: 5% m/z 367: 4%	m/z 117: 5% m/z 135: 3%
Al ₈			m/z 196: 9% m/z 205: 9% m/z 409: 6% m/z 427: 5%		m/z 167: 12%	m/z 167: 7%
Al ₉			m/z 226: 15%			m/z 453: 7%
Al ₁₀			m/z 256: 11% m/z 511: 6%	m/z 265: 11% m/z 274: 12% m/z 283: 9% m/z 529: 6%	m/z 165: 14%	m/z 165: 8%
Al ₁₁		m/z 286: 7%	m/z 349: 23% m/z 358: 17% m/z 367: 21% m/z 553: 8%			
Al ₁₂		m/z 298: 20% m/z 307: 10%	m/z 298: 36% m/z 307: 20% m/z 316: 8%			
Al ₁₃		m/z 213: 10% m/z 219: 9% m/z 328: 21% m/z 337: 11% m/z 355: 6%	m/z 213: 33% m/z 328: 61% m/z 337: 30%	m/z 213: 16% m/z 219: 15% m/z 225: 9% m/z 328: 56% m/z 337: 100% m/z 346: 18% m/z 355: 16% m/z 364: 10%	m/z 219: 5% m/z 328: 18% m/z 337: 33% m/z 346: 5% m/z 355: 6% m/z 364: 4%	m/z 328: 12% m/z 337: 23%
Al ₁₄			m/z 233: 15%	m/z 233: 10% m/z 358: 47%	m/z 245: 7% m/z 358: 24%	m/z 358: 16%
Al ₁₅			m/z 379: 7% m/z 388: 7%	m/z 379: 33% m/z 388: 6%	m/z 379: 14%	
Al ₁₆				m/z 400: 16% m/z 418: 10%	m/z 400: 11% m/z 409: 5% m/z 418: 6% m/z 427: 4%	m/z 400: 8% m/z 418: 5%
Al ₁₉		m/z 321: 6%	m/z 321: 10%			
Al ₂₁				m/z 373: 10%		
Impurity	m/z 183: $[\text{TMA}_2\text{Cl}]^+$; m/z 261, 335: $[\text{K}(\text{KCl})_3-4]^+$; m/z 245, 319: $[\text{Na}(\text{KCl})_3-4]^+$					

polymerized into small polymeric aluminum species (Al₃, Al₄ and Al₅ species, Fig. 1b). Through aggregation and self-assembly, the small polymeric aluminum species easily polymerized into me-

dian polymeric species (e.g. Al₈, Al₉ and Al₁₀ species, Fig. 1c). In the same way, small and median polymeric aluminum species further aggregated into large polymeric species (e.g. Al₁₂, Al₁₃ and

Al₁₄ species, Fig. 1d). This compares favorably with the results of Bottero et al. [19] and Arnson [20] reported the existence of polymeric K-Al₁₃ and Al₈ species at low concentration in weak acidic pH range. The median and large polymeric aluminum species may be transient and metastable hydrolysis–polymerization products. When pH was up to 5.8, transient median and large polymers species decomposed into small aluminum species, then further disaggregated into dimeric species (Fig. 1e). With pH increased to 6.4, majority of aluminum species formed to Al(OH)₃ amorphous flocs. Summarizing the above discussion, hydrolysis of aluminum salts, at a low concentration (normal dose of coagulant), included polymerization and decomposition processes.

In contrast to AlCl_3 , K-Al_{13} species coagulant PACI had a similar formation and decomposition process. K-Al_{13} species were stable polymeric aluminum species, so their formation and decomposition conditions were particular. It is well established that aluminum solution can lead to the polymerization of K-Al_{13} rapidly and irreversibly under specific conditions [11,24]. Thus, coagulant PACI with high content of K-Al_{13} can be preformed in the research and coagulation process [6,22]. Particularly, some investigations indicated that preformed K-Al_{13} species were not stable at certain conditions, and they also can decompose into Al^{3+} [25]. The formation and decomposition of K-Al_{13} in PACI needs rigorous conditions, hence cannot occur during coagulation.

There are two main mechanisms of aluminum salts hydrolysis, which include the “Core-link” model and the “Cage-like” model. “Cage-like” model (K-Al₁₃ structure) holds that in aluminum solutions there are only monomer, dimer, K-Al₁₃ polymer, and larger polymerized aluminum species. These species can be transformed from one to another directly [19,21]. The “Core-links” model gives a distribution of continuously changed species from aluminum hydrolysis production following the hexameric ring model [7,8]. Therefore, many possible polynuclear species can be interpreted in this model. However, there is no unification between the two widely models.

In this study, although the formation conditions of polymeric aluminum were different, both AlCl_3 and PACI had similar processes of polymeric aluminum species formation and decomposition. On one hand, the K-Al_{13} is formed by the structural reshuffle of transient polymeric species after aging. The changing process is the transient polymeric aluminum from disorder to order. The formation of stable K-Al_{13} in PACI coagulant was based on the “Cage-like” model. On the other hand, the hydrolysis polymerization of aluminum salts during coagulation followed the “Core-

links" model. Therefore, the "Core-links" model and the "Cage-like" model could be unified.

4. Summary

This work examined the effect of pH on the AlCl_3 hydrolysis at low concentration (1.5×10^{-4} mol/L). Using the ESI-MS measurement, the formation and decomposition of polymeric aluminum species were demonstrated. With pH increasing, monomeric and dimeric aluminum species polymerized into small polymeric aluminum species. Through aggregation and self-assembly, the small polymeric aluminum species polymerized into median polymeric species, then further aggregated into large polymeric species. The median and large polymers species was not stable, could decompose into small aluminum species, then formed $\text{Al}(\text{OH})_3$ amorphous flocs.

Based on the above results, coagulant hydrolysis mechanism from polymerization toward decomposition was proposed. Therefore, the “Core-links” model and the “Cage-like” model could be unified.

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Supporting material

The online version of this article contains additional supporting material.

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