Aluminum speciation of coagulants with low concentration: Analysis by electrospray ionization mass spectrometry

He Zhao, Huijuan Liu, Jiuhui Qu

Abstract

Aluminum speciation of coagulants with low concentration was investigated in detail by electrospray ionization mass spectrometry (ESI-MS). In particular, comparison with $^{27}$Al nuclear magnetic resonance ($^{27}$Al NMR) and Ferron colorimetric method for aluminum speciation of coagulants was discussed. The results indicated that various hydrolyzed aluminum species (monomeric, dimeric, trimeric and tetrameric aluminum species), which could not be identified by other methods, appeared in ESI-MS spectra. Thus, ESI-MS method was much better for hydrolyzed aluminum species in low concentration. In this paper, sample cone voltage was an important operating parameter during ESI-MS detection, and optimum voltage was 70 V. Too low (40 V) or high (150 V) sample cone voltage was not suitable for detecting all aluminum species. This study also evaluated the effects of coagulant concentration, aging, pH value and organic matter on aluminum species distribution. The results indicated that the distribution of hydrolyzed aluminum species at low concentration was largely dependent on the solution pH. At higher pH conditions, aging (8–12 h) may influence aluminum hydrolysis. Additionally, after adding salicylic acid into coagulant solutions, speciation and stability for both Al$_{13}$ species and aluminum–salicylate complexes varied significantly at different pH values.

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 nuclear magnetic resonance ($^{27}$Al NMR) spectroscopy [7,8]. In addition, X-ray diffraction [9], Raman spectroscopy [10] and X-ray photoelectron spectroscopy [11] 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$_{13}$, AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$) species [12]. However, investigations on speciation of aluminum salts at low concentrations in nature and coagulation are hampered by the detection limits of $^{27}$Al NMR. Therefore, based on detecting mass to charge ratio (m/z) of complexes, the ESI-MS measurement has been proved as an useful probe for the determination of aluminum species.

Recently, Sarpola [13] applied a well established method to aluminum complexes using electrospray ionization mass spectrometry (ESI-MS) in his PhD thesis. Researchers [14–17] emphatically analyzed and identified hydrolysis products of aluminum chloride (AlCl$_3$) at different concentrations by ESI-MS method. Later, aluminum salts in the presence of sulfate [18], nitrate/perchlorate [19] and acetoni trile [20] were investigated by ESI-MS. Furthermore, Rämö et al. [21] demonstrated that aluminum speciation variation of the polyaluminum chloride (PACl) with high and medium basicity 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 an useful probe for the determination of aluminum species.

As common coagulants, AlCl$_3$ and PACl are widely used in water treatment process [22,23]. Due to coagulation efficiency controlled by in situ hydrolyzed coagulant species after dosing, scientists have done much research focuses on the aluminum speciation of the coagulants [1,2,24]. In various studies, many factors exhibit effects on the speciation of coagulants at low concentration. Wang et al.
[6] and Hu et al. [22] investigated the influences of concentration, pH and aging by Al–Ferron assay. However, owing to the limit of Al–Ferron method, hydrolyzed aluminum species at low concentrations were difficult to be identified accurately. Therefore, it is valuable that if ESI-MS method can be used in analyzing speciation of Al hydrolysis at low concentration. Furthermore, effects of factors (concentration, aging, pH and organic matter) on hydrolyzed aluminum species at low concentration using ESI-MS method still need further investigation.

The primary objective of the present research was to analyze aluminum speciation for coagulants with low concentration by ESI-MS. The effect of sample cone voltage, an important operating parameter, on aluminum species distribution during ESI-MS detecting was investigated in detail. The results of ESI-MS method were compared with 27Al NMR and Al–Ferron methods. The effect of coagulant concentration, pH, aging and organic compound on aluminum speciation was also investigated.

2. Materials and methods

2.1. Characterization of coagulants

AlCl3·6H2O (Guaranteed Reagent, Beijing Chemical Regents Company) and a commercial PACI (PACI1, Nanning Chemical Industry Co. Ltd., China) were used in this study. Besides, another PACI (PACI2) was prepared with the method of an electrolysis process [25,26]. Total aluminum concentrations (AlT) were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 2000, Perkin Elmer, U.K.). Basicity values (B, OH/Al molar ratios) were determined by titrimetric methods (standard chemical industry of China).

Aluminum speciation of coagulant was characterized by a 27Al NMR spectroscopy (500 MHz, Varian Unity Inova, USA). Samples were placed in 5-mm tubes and the spectra were generated at 25 °C. To estimate the distribution of various species in solution, selected samples and standard solutions of known monomeric Al concentration were run using a coaxial sample tube, with a 0.2 mol/L sodium aluminate solution in the inner insert as reference. The intensities at 0 and 4.3 ppm resonances, respectively, represented the quantitative determinations of monomeric Al and dimeric Al, which named as Alm. The peak at 63 ppm resonance represented Keggin-Al13 polymer in aluminum solution, and 80 ppm resonance represented sodium aluminate. The difference between AlT and [Alm +Al13] was an undetected part (Alu, i.e., larger polymer species and/or solid-phase Al(OH)3) by 27Al NMR.

The Ferron colorimetric method was also used to analyze Al species distributions of the coagulants. Details of the operating approaches can be found in the literature [22]. Three categories of species, Alm, Alb and Alc were analyzed by Al–Ferron assay, which were corresponding to monomer, medium polymer, and larger polymer species and/or solid-phase Al(OH)3, respectively.

2.2. ESI measurements

The ESI time of flight (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 with a positive ion mode. The solutions were introduced into the spectrometer at a flow-rate of 10 μL/min. The instrumental conditions were as follows: capillary voltage 3500.0 V, cone gas (N2) flow rate 300 L/h, mass range 80–1000.

In our experiments, to investigate aluminum speciation of the coagulant after dosing, the coagulant was diluted to low concentrations (1.5×10−4 mol/L). 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. To further investigate effect of organic compound on aluminum speciation, salicylic acid (Guaranteed Reagent, Beijing Chemical Regents Company) was used as model compound in this study, and the concentration was kept at 1.5×10−4 mol/L. Tetramethylammonium hydroxide pentahydrate (CH3)4NOH·5H2O (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). Deionized water was used to provide baseline species distributions data.

3. Results and discussion

3.1. Comparison between ESI-MS and other methods for Al speciation

The characteristics of coagulants and aluminum speciation analyzed by 27Al NMR and Al–Ferron assay were presented in Table 1. In order to analyze hydrolyzed aluminum species at low concentrations accurately, ESI-MS was used to detect the aluminum speciation of the coagulants at [AlT]=1.48×10−4 mol/L. As shown in Fig. 1 and Table 1, differences of aluminum speciation between AlCl3 and PACI were significant. For AlCl3 (0.55 mol/L), 27Al NMR spectrum indicated that AlCl3 was 100% Alm (including monomeric Al and dimeric Al). Ferron colorimetric results also demonstrated that Alm were dominant species in the AlCl3 solution. Although Al–Ferron assays were used at low concentrations, aluminum species were only roughly classified as Alm, Alb and Alc. Thus, it suggested that dominated species of AlCl3 were monomeric Al or dimeric Al by combined 27Al NMR with Al–Ferron. However, as illustrated in Fig. 1a, when total aluminum concentrations of the coagulants were diluted to normal dosage at low concentration, various hydrolyzed Al species of AlCl3 appeared in ESI-MS spectra. Majority of signals appeared in the ESI-MS spectra and possible aluminum species are summarized in Table 2. The most intensive peaks were assigned to dimeric aluminum species at m/z 103, m/z 121, m/z 139, m/z 157 and m/z 175 ([Al2O2(OH)(H2O)6]4+). Monomeric aluminum species ([Al(OH)2(H2O)2]3+) at m/z 97, trimers ([m/z 181, 199, 217 and 235]), tetramers ([m/z 87, 105, 123 and 277]) and Al13 species ([m/z 328 and 337]) were also observed in the spectra. Various hydrolyzed Al species of AlCl3, like monomeric, dimeric, trimeric and tetrameric aluminum species, which could not be identified by traditional methods, can be detected by ESI-MS. By evaluated semi-quantitatively, dimers were major aluminum species, and a few high polymeric species formed.

### Table 1: Characteristics of coagulants and aluminum speciation by 27Al NMR and Al–Ferron assay.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Alm (mol/L)</th>
<th>pH</th>
<th>Al speciation (%)</th>
</tr>
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<tbody>
<tr>
<td>AlCl3</td>
<td>0.55</td>
<td>0</td>
<td>2.21 100</td>
</tr>
<tr>
<td>PACI1</td>
<td>0.64</td>
<td>1.5</td>
<td>2.78 48.8</td>
</tr>
<tr>
<td>PACI2</td>
<td>0.53</td>
<td>2.1</td>
<td>4.57 0</td>
</tr>
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</table>

3: B: basicity values (OH/Al molar ratios).
Alm: monomeric Al and dimeric Al, Alu was an undetected part by 27Al NMR, Alm = Al − [Alm + Al13].
4: The reaction time of Alam and Ferron reagent was 1 min; the aluminum species reacting with the Ferron reagent before 120 min represented [Alm + Alb]; Alc = Al − [Alm + Alb].
For PACl1 (0.64 mol/L), the results from 27Al NMR spectra were in good accordance with those from Ferron method. The contents of Alm (Al1), Al13 (Alb), and Al6 (Alc) were 48.8% (43.0%), 34.8% (37.4%) and 16.4% (19.6%), respectively. A little different from 27Al NMR and Ferron results, ESI-MS results indicated that coagulant PACl1 at low concentration had many Al13 species and a few Al2 species. As shown in Fig. 1b, Al13 species ([Al13O18(OH) (H2O)0–4]2+) at m/z 328, m/z 337, m/z 346, m/z 355, m/z 364, m/z 213, m/z 219, m/z 225 and m/z 237 were dominated in the spectra. Dimeric aluminum species (m/z 121, 139, 157 and 175), Al14 species (m/z 233, m/z 358) and Al15 species (m/z 379) were also observed. For PACl2 (0.53 mol/L), Keggin-Al13 (Alb) was dominant species in the PACl2 solution. By 27Al NMR and Ferron detecting, the content of Keggin-Al13 and Al6 was 81.2% and 80.6%, respectively. It is consistent with the results of ESI-MS at low concentration. In Fig. 1c, Al13 polymers (m/z 213, m/z 219, m/z 225, m/z 238, m/z 337, m/z 346, m/z 355, m/z 364) were dominated aluminum species in PACl2. Additionally, Al14 species (m/z 233, m/z 358) and Al15 species (m/z 379) were observed as well.

### Table 2

Majority of signals in the ESI-MS spectra and possible aluminum species.

<table>
<thead>
<tr>
<th>Signals (m/z)</th>
<th>Primary ion</th>
<th>Species</th>
</tr>
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<tr>
<td>79, 97</td>
<td>[Al(OH)2(H2O)2]6+</td>
<td>Al1</td>
</tr>
<tr>
<td>103, 121, 139, 157, 175</td>
<td>[Al3O18(OH)4(H2O)4]6+</td>
<td>Al3</td>
</tr>
<tr>
<td>145, 163, 181, 199, 217, 235</td>
<td>[Al5O10(H2O)6]6+</td>
<td>Al5</td>
</tr>
<tr>
<td>247</td>
<td>[Al4O10(H2O)6]6+</td>
<td>Al4</td>
</tr>
<tr>
<td>298</td>
<td>[Al5O12(H2O)6]6+</td>
<td>Al5</td>
</tr>
<tr>
<td>232</td>
<td>[Al5O12(OH)6]6+</td>
<td>Al5</td>
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<td>348, 358</td>
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<td>379</td>
<td>[Al5O12(OH)4]6+</td>
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</tr>
<tr>
<td>113</td>
<td>[K2Cl]+</td>
<td>Impurity</td>
</tr>
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</table>

### 3.2. Effect of sample cone voltage on the ESI-MS analysis

During ESI-MS detecting, aluminum ions were transferred from solution to the gas phase by electrospray, where the aluminum ions can be examined semi-quantitatively by conventional mass spectrometric techniques. Previous study indicated that hydrolyzed aluminum species appeared in ESI-MS spectra were not fragments that evolved during ionization or detection. For standard electrospray, ionization of aluminum species is very important [13]. Thus, the optimum operating condition of electrospraying was that most hydrolyzed aluminum species were ionized in the solution. In the study of coagulants with low concentration, the ESI-MS operating conditions were tested and sample cone voltage was the most important parameter. The spectra of AlCl3 with different sample cone voltages at pH 3.8 and pH 4.4 are shown in Figs. 2 and 3, respectively. At pH 3.8, the spectra of aluminum species at 40 V and 70 V were similar with each other. However, spectrum of aluminum distribution at 150 V was a little different from that at 40 V (or 70 V). Many aluminum species disappeared at higher sample cone voltage, and total ion count (TIC) diminished at 150 V. Aluminum species at m/z 97, 121 decreased, but impurity peak at m/z 113 was increased. Furthermore, some new species appeared, e.g. Al4 species at m/z 277 and 295. When pH was increased to 4.4, undetected species by ESI-MS (e.g. amorphous Al(OH)3 flocs) formed and total ions decreased. The spectra of aluminum species at 40 V, 70 V and 150 V were different from each other. At 150 V, impurity peak at m/z 113 ([K2Cl]+) was significant (potassium is an impurity that may originate from aluminum solutions), but almost all aluminum species were undetected. As shown in ESI-MS spectrum at 40 V, comparing to monomer at m/z...
Fig. 2. ESI-MS spectra of fresh AlCl₃ coagulant (1 × 10⁻⁴ mol/L) at pH 3.8 with sample cone voltage of (a) 40 V; (b) 70 V; (c) 150 V.

79 and dimer at m/z 139, impurity peak at m/z 113 was diminished. However, only a few aluminum species can be detected at low sample cone voltage. At 70 V, though impurity peak at m/z 113 increased, more hydrolyzed aluminum species can be detected by ESI-MS. Peak at m/z 79, 97 and at m/z 103, 121, 139, 157, 175 were assigned as monomers [Al(OH)₂(H₂O)⁻₂]⁺ and dimers [Al₂O₂(OH)(H₂O)₄⁻⁴]²⁻, respectively. Trimers [Al₃O₄(OH)(H₂O)₆⁻₆]⁻ at m/z 181, 199, 217, 235, 253 and [Al₁₃O₁₈(OH)(H₂O)₀⁻¹]²⁺ at m/z 380, 360, 340, 320, 300, 280, 260, 240, 220, 200, 180, 160, 140, 120, 100, 80, 60, 40, 20, 0.

Fig. 3. ESI-MS spectra of fresh AlCl₃ coagulant (1 × 10⁻⁴ mol/L) at pH 4.4 with sample cone voltage of (a) 40 V; (b) 70 V; (c) 150 V.
3.3. Effect of pH on Al speciation

As illustrated in Figs. 4 and 5, pH had a significant effect on aluminum speciation. With pH increase, aluminum hydrolysis was accelerated. At pH 4.6 (Fig. 5a), dimers ([Al2O2(OH)(H2O)0–4]+ at m/z 103, 121, 139, 157, 179) and trimers ([Al3O4(OH)Cl(H2O)0–3]+ and [Al3O3(OH)2Cl(H2O)0–2]+ at m/z 145, 163, 181, 199, 217, 235) were the dominating species. In addition, series of polymers containing Al4 (m/z 223, 241, 259 and 277), Al5 (m/z 247) and Al13 (m/z 328 and 337) were observed as well.

When pH increased to pH 5.0 (Fig. 5a), dimers and trimers decreased to less, but Al4 (m/z 277), Al5 (m/z 247), Al12 (m/z 298) and Al13 (m/z 213, 238 and 337) species increased to be dominant species. That is, the distribution of hydrolyzed aluminum species was largely dependent on solution pH conditions. Higher pH can cause that aluminum species further hydrolyzed. Thus, pH can significantly accelerated aluminum hydrolysis. Our previous study also indicated that effect of pH on aluminum speciation was very important in aluminum hydrolysis [16], especially for traditional coagulant during coagulation [30,31].

3.4. Effect of aging on Al speciation

Aging time (8–12 h) was another important factor which influenced the distribution of hydrolyzed aluminum species, but its effect was largely dependent on solution pH conditions. At pH 4.6, aging did not affect distribution of hydrolyzed aluminum species. As illustrated in Fig. 4, hydrolyzed aluminum speciation in fresh solution was similar with that in aged 8 h and 12 h solution.

However, when pH was increased (pH 5.0), undetected species by ESI-MS (e.g. amorphous Al(OH)3 flocs) formed more easily and total ions decreased in aged solution (8–12 h). Many hydrolyzed aluminum species appeared in fresh solution did not observe in aged solution. That is, the aluminum species in fresh solution were still in hydrolysis. Previous research [6,32] indicated that aluminum species underwent structure rearrangement with aging. Wang et al. [6] used Ferron method to demonstrate that aging promoted particle aggregation and formation of amorphous hydroxide precipitates with increase of the solution pH. In this study, structure rearrangement occurred spontaneously in aged solution. Thus, with pH increase, hydrolysis was accelerated and formed undetected species (finally into Al(OH)3 flocs). Accordingly, at higher pH conditions, aging (8–12 h) could influence aluminum hydrolysis.

3.5. Effect of organic matter on Al speciation

The effect of organic matter on the distribution of aluminum species was investigated by ESI-MS method and the results were presented in Fig. 6. Fragment ions and proposed complexes inferred...
Fig. 5. ESI-MS spectra of AlCl₃ coagulant (1 × 10⁻⁴ mol/L, sample cone voltage 70 V) at pH 5.0; (a) fresh solution; (b) aged 8 h solution; (c) aged 12 h solution.

from Fig. 6 spectra were summarized in Table 3. At pH 4.0 (Fig. 6a), Al₁₃ polymers [Al₁₃O₁₈(H₂O)₀–₂]³⁺ (m/z 213, 219, 225) and [Al₁₃O₁₈(OH)(H₂O)₀–₃]²⁺ (m/z 328, 337, 346, 355) still were dominated aluminum species in the spectra. Additionally, monomeric species (m/z 97), dimeric species (m/z 121) and trimeric species (m/z 181, 191) were observed as well. In the spectrum, Al₁₃Lₙ complexes (L means salicylic acid ligand, n = 1–3), which formed by Al₁₃ species and salicylic acid, were major complexes, e.g. Al₁₃L (m/z

Fig. 6. ESI-MS spectra of fresh PACl₂ ([Al₁₃] = 1.5 × 10⁻⁴ mol/L) with salicylic acid (1.5 × 10⁻⁴ mol/L), sample cone voltage = 70 V; (a) pH 4.0; (b) pH 5.0; (c) pH 6.0.
Fragment ions and proposed complexes inferred from Fig. 6 spectra, PACl2 ([Al] = 1.5 × 10^{-4} mol/L), salicylic acid (1.5 × 10^{-4} mol/L), pH 4.0–6.0.  

<table>
<thead>
<tr>
<th>m/z</th>
<th>Primary ion</th>
<th>Species</th>
<th>Formula</th>
<th>Molecular weight</th>
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* M = molecule before ionization, H = proton, L = salicylic acid ligand.

(1) Various hydrolyzed monomeric, dimeric, trimeric and tetrameric aluminum species could be analyzed by ESI-MS method. Compared with $^{27}$Al NMR and Ferron method for difficult to identify aluminum species at low concentrations accurately, ESI-MS was much better.

(2) Sample cone voltage was an important operating parameter for analysis of aluminum speciation by ESI-MS. 70 V has been found as optimum sample cone voltage.

(3) The distribution of hydrolyzed aluminum species was largely dependent on solution pH, aging time and organic matter. The Al_{13} species could react with salicylic acid to form Al_{13}–salicylate complexes or decompose directly into oligomeric aluminum species. With pH increase, Al_{13} species and newly formed Al_{13}–salicylate complexes were not stable in the presence of salicylic acid, only oligomeric aluminum species and oligomeric–salicylate complexes could be detected.

Acknowledgement

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References


