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Quantification analysis of polymeric Al species in solutions with electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS)

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ABSTRACT

With the help of Ferron colorimetric method and ^{27}Al NMR spectroscopy, quantification analysis method of electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) on Al speciation was developed and thus Al species in polymeric Al solutions were quantitatively analyzed. Based on the speciation results of mononuclear Al solution and purified Al_{13} solution, Al species obtained with ESI-TOF-MS in polymeric Al solutions were classified into three categories as low polymers (i.e., Al_1–Al_{10}), mid polymers (i.e., Al_{13}–Al_{20}), and high polymers (i.e., Al_{21}–Al_{31}). Among these polymers, only a certain number of Al species have relative high content and constitute the dominant component of polymeric Al solutions. The quantification analysis results of ESI-TOF-MS agree well with those obtained by the other two traditional methods, which proves the feasibility of the novel method on Al species analysis. Additionally, ESI-TOF-MS can provide more information on Al speciation than ^{27}Al NMR spectroscopy and Ferron colorimetric method, and the quantification analysis results can clearly explain the difference between the two traditional methods.

1. Introduction

Over the past few decades, hydroxyl Al speciation has been proved to greatly affect the application of Al salt products in water treatment, catalysis, cosmetic science, geochemistry, etc. [1–3]. To synthesize the products with high content of high-performance Al species in these fields, many attempts have been made to prepare prehydrolyzed Al products and characterize Al species in solutions [4,5]. Owing to the complexity of polymeric Al species and the shortage of efficient methods on Al speciation, the existing categories and transformation pattern of Al species are still in controversy [6,7]. To fully recognize hydroxyl Al species, especially their quantification distribution in solutions, is still the focus for many researchers all over the world nowadays.

In recent years, electrospray ionization mass spectrometry (ESI-MS) with different mass analyzer has been used to characterize chemical species of Al in solutions [8–10]. From the distribution characteristics and m/z values of peaks in mass spectrum, various Al species with different polymerization degree can often be identified. Moreover, the possible molecular structure of Al species can also be deduced with a general formula suggested by different researchers [8,9]. Since ESI mass spectrometry was often considered as a mild ionization method, Al species in original solution might have minor changes when they were transferred into gas phase to be measured in mass analyzer [11–13]. Electrospray ionization mass spectrometry has exhibited strong potential in the analysis of hydroxyl Al species.

Heretofore, most studies on Al speciation with ESI mass spectrometry have put emphasis only on the identification of Al species from mass spectra [14,15]. However, great controversy still existed between different researchers on the Al species identification results in mass spectrometry [15–18]. The main reason is that most studies only focused on the application of mass spectrometry and less attention has been paid to the additional explanation of some traditional methods. Thus the differences in Al speciation results obtained in different studies cannot be well explained.

In fact, the qualitative analysis results are not enough to explain Al speciation in solutions. Many researchers have tried to quantify Al species with ESI mass spectrometry. Zhao and Urabe analyzed the difference in the relative intensities of peaks for various Al species identified from mass spectra [16,17]. Rämö summed the signal intensities of oligomeric Al species and took them as total ion counts to evaluate the abundance in solutions [18]. They have only tried the semi-quantitatively study on Al species in solutions with ESI mass spectrometry, and the qualitative results were not simultaneously approved with some traditional methods. On the whole, studies on the quantification analysis of Al species with ESI

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mass spectrometry are still in an initial stage and there is still lack of feasible analysis method.

Many chemical and instrumental methods have been adopted to analyze hydroxyl Al species in solutions. ^{27}Al NMR spectroscopy and Ferron colorimetric method are the two most commonly used methods [19,20]. ^{27}Al NMR spectroscopy has been widely recognized as the sole instrumental method to identify the Al species directly, though only a few Al species (i.e., Al_m, Al_2 even Al_3, Al_{13}, and Al_{30}.) can be observed. As for Ferron colorimetric method, it can only give only a rough classification without any actual species in each category. Perhaps, the simultaneous application of the above two methods could provide additional explanation for the identification and quantification analysis results of hydroxyl Al species in ESI mass spectrometry. Therefore, with the help of the above two methods, the aim of this study is to establish a relative perfect quantification analysis method of ESI-TOF-MS for hydroxyl Al species in solutions, and thus Al species in polymeric Al solutions will be identified and discussed quantitatively to further clarify their transformation process.

2. Materials and methods

2.1. Synthesis of hydroxyl Al solutions

Deionized water was used to prepare all the solutions and all the reagents were analytical grade chemicals. Hydroxyl Al solutions were made via the micro-titrating method. Under rapid stirring and bubbling with N_2 gas, a calculated volume of 0.27 M $AlCl_3$ solution was titrated slowly with 0.5 M NaOH solution by using a titrometer (665 Dosimat, Metrohm, Switzerland). The addition rate was 0.15 mL min^{-1} and the volumes added varied with the target B values (OH/Al molar ratios) which were chosen as 0, 0.5, 1.0, 1.5, 2.0, 2.2, and 2.5, respectively. The resulting samples were denoted respectively as PAC_0, PAC_{05}, PAC_{10}, PAC_{15}, PAC_{20}, PAC_{22} and PAC_{25}. The purified Al_{13} sample (simplified as PAl_{13}) was obtained from PAC_{22} by the method of chemical purification [21]. The final concentration of total Al (Al_T) in every sample was adjusted to about 0.1 M with deionized water. Exact Al concentrations were measured with ICP-OES (PerkinElmer Co., USA). The samples were aged for 24 h at room temperature before they were preserved at 4 °C for analysis.

2.2. Electrospray ionization time-of-flight mass spectrometry

Mass spectra were recorded with a high performance liquid chromatography/hybrid quadrupole time-of-flight mass spectrometer (Micromass Q-ToF Micro, Waters, USA). The samples were injected into the spectrometer at a flow rate of 10 μL/min. The instrumental conditions were as follows: capillary voltage of 3500.0 V, sample cone voltage of 70 V, Fflens of 200 V, extraction cone voltage of 5 V, source temperature of 120 °C, cone gas (N_2) flow rate of 300 L/h, and mass range of 80–1000. All the ESI mass spectra were observed in positive ion mode.

2.3. ^{27}Al NMR spectroscopy

The samples were studied with 500 MHz ^{27}Al NMR (Brookhaven Co., USA). The instrumental settings and experimental conditions were: NS = 128, P1 = 20 μs, $Al(OD)_4^-$ PL1 = −3 dB. Solvent: D_2O, and $T = 298$ K. The inner standard was 0.05 M solution and its chemical shift is 80 ppm. The signals near 0, 3–4 and 62.5 ppm represent monomers (Al_m), dimers (Al_2) and Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$), respectively. The concentration of each species was determined by the ratio of the integrated intensity of its corresponding peak to that of $Al(OD)_4^-$ at 80 ppm. The amount of the undetectable species (denoted as Al_{un}) was obtained by subtracting the sum of the detected Al species from the Al_T concentration in each sample.

2.4. Ferron colorimetric method

Ferron colorimetric solution was obtained by mixing the Ferron solution (0.2%, w/v), NaAc solution (20%, w/v), and HCl solution (1:9, v/v) at a ratio of 2.5:2:1. The detailed procedure for the preparation of Ferron solution was same as that in [5,22]. For the speciation of each sample, 5.5 mL Ferron colorimetric solutions were first transferred into a graduated glass tube and diluted to 25 mL. Then, 20 μL test Al solutions were added to the tube and the reaction time was recorded simultaneously. After homogeneous mixing, the reacting sample was quickly added to a 1–cm quartz cell. The absorbance changes, using a UV–vis 8500 spectrophotometer (Tianmei Co., China), were monitored automatically at 366 nm from 30 s to ca. 2 h until no detectable absorbance increase was observed, indicating the completion of the reactions between the mononuclear Al (Al_a) and reactive hydroxyl Al polymers (Al_b) with Ferron. The residual species that cannot react with Ferron in the limited time is defined as Al_c (i.e., inert high polymers or colloidal Al species). The content of Al_c can be obtained by the difference between the content of $Al_a + Al_b$ and that of Al_T in solutions [22].

3. Results and discussion

3.1. Quantification analysis method of mass spectrometry on Al speciation

A general formula $[Al_xO_y(OH)_z(H_2O)_m]^{(2y+z-3x)+}$ was suggested for the identification of Al species from mass spectra. For simplicity, Al_x was used in the following sections to denote species with the same polymerization degree x and the same charge $(2y+z-3x)+$. As shown in Fig. 1, Al species with the same polymerization degree are often observed as some peaks with different m/z values in mass spectrum and these peaks often constitute a Gaussian-shaped cluster [13,23]. Thus, in order to quantify Al species in solutions, the first, and the most important step is to determine the m/z scope of every cluster in mass spectrum.

The difference in m/z values of peaks in a cluster are often ascribed to the exchange of water molecular (or oxo and hydroxo ligands) in the structure of Al complex [14,16]. As inferred from our former studies (not shown), the fragmentation or coordination of water molecular resulted in the difference of peaks in a Gaussian-shaped cluster with higher m/z values in mass spectrum. However, the difference of peaks in clusters with lower m/z values are mainly ascribed to the changes of oxo and hydroxo ligands in the structure of Al complex. The distribution characteristics of peaks could be used as the first principle to determine the m/z scope of Gaussian-shaped clusters.

According to the chemical theory of hydroxyl Al structure, the number of ligands in a hydroxyl Al complex should be limited to a certain range. Moreover, mass, charges and even structure of Al species can be inferred from the distribution characteristics of peaks. Thus, the characteristics, especially the number of ligands, of hydroxyl Al structure could be taken as the second principle for the determination of the corresponding m/z scope of every Gaussian-shaped cluster.

Additionally, polymerization degree of Al species identified from peaks often increases with m/z value in mass spectrum [8,10]. The well correspondence provides another way to determine the m/z value scope of every Gaussian-shaped cluster in mass spectrum. Moreover, the continuity of changes in polymerization degree of Al species with m/z value can also be used to solve the problem that one m/z value could be assigned as two different Al species. Thus,

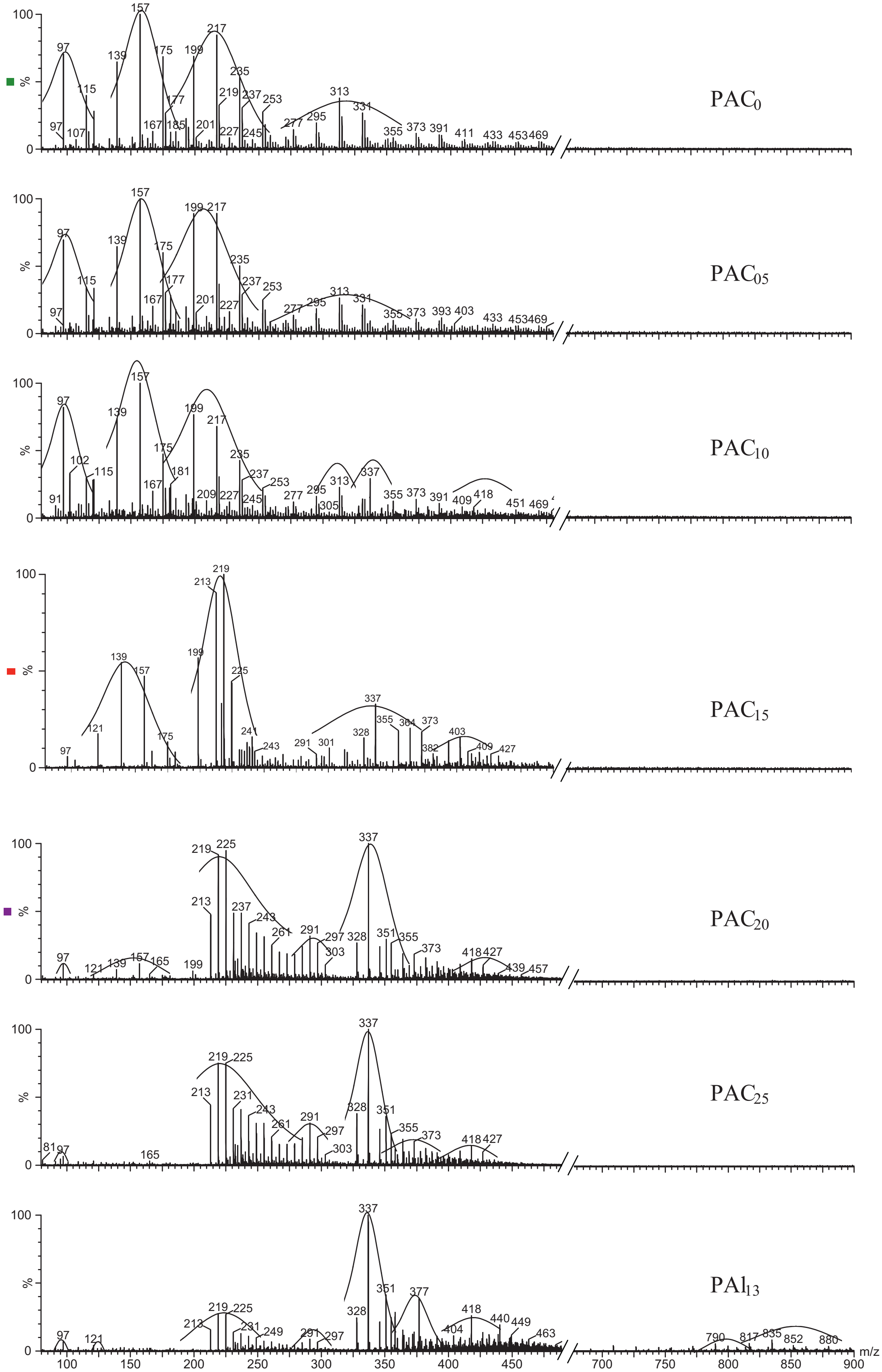

Fig. 1. ESI-TOF mass spectra of hydroxyl Al solutions with different basicity (PAC$_0$, PAC$_{05}$, PAC$_{10}$, PAC$_{15}$, PAC$_{20}$, PAC$_{25}$, and PAl$_{13}$).

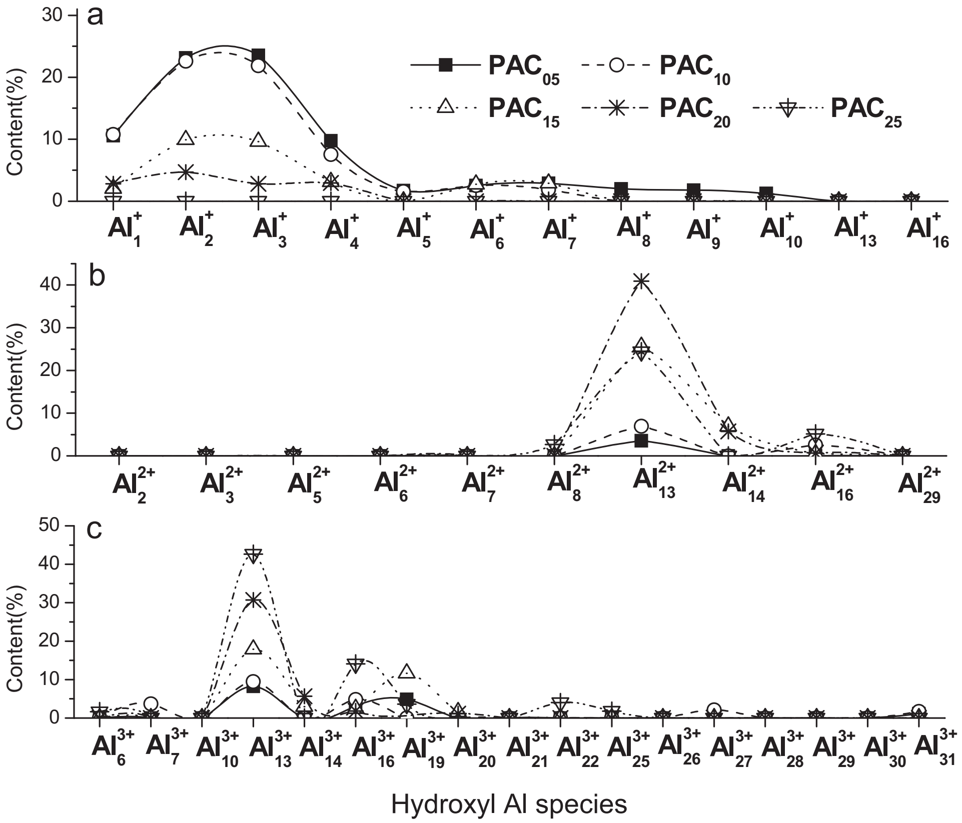

Fig. 2. Quantification analysis results of Al species with one (a), two (b) and three charges (c) in polymeric Al solutions (PAC_{05}, PAC_{10}, PAC_{15}, PAC_{20}, and PAC_{25}) with ESI-TOF mass spectrometry.

the distribution characteristics of Gaussian-shaped clusters with *m/z* values in mass spectrum can be taken as the third principle to determine the *m/z* scope of Gaussian-shaped clusters.

After the determination of the *m/z* scope of every cluster, the second step is to calculate the total intensity of Al species assigned from every Gaussian-shaped cluster. Then, the relative content of Al species identified from mass spectra can be easily obtained by the ratios of the intensity of every Al species to that of the whole species in samples. The main theoretical basis of the above calculation is the fact that the relative intensity of peaks observed in mass spectrum is in accordance with the content of the corresponding Al species in solutions [11,12].

3.2. Distribution of Al species identified from mass spectra of polymeric Al solutions

Mass spectra of hydroxyl Al solutions were shown in Fig. 1. Only part of mass spectrum with obvious peaks was shown in the figure for each sample. The other part of mass spectra often had high signal-to-noise ratios and no obvious peaks were detected on them. Since only one dominant peak was observed in each mass spectrum, the peak was often taken as the base peak and the intensity of the other peaks were then obtained by the normalization to the intensity of the base peak [13].

In this study, only the peaks with relative intensity over 5% of that of the base peak were considered. The ignorance of the peaks with lower intensity was mainly ascribed to the uncertainty to distinguish them from noise. Besides the peaks with lower intensity, almost all the other peaks in each mass spectrum in Fig. 1 were analyzed. Al species with the same polymerization degree have been categorized as one species Al_x and the total intensity was also summed. The detailed *m/z* values of various Al species can be clearly obtained from peaks in every Gaussian-shaped cluster in Fig. 1 (e.g., Al_{13}^+ at *m/z* 709 ± 18, Al_{13}^{2+} at *m/z* 337 ± 9, andAl_{13}^{3+} at *m/z* 219 ± 6).

Fig. 2 shows the content distribution of Al species in polymeric Al solutions with different basicity in mass spectrometry. Three groups of Al species with different charges were observed in Fig. 2a–c, respectively. Only three kinds of charges (+1, +2 and +3) were carried by the species in mass spectrometry [8–10]. It can be seen from Fig. 2 that more categories of Al species carry three charges (+3). Since Al species (e.g., Keggin-Al_{13}^{7+}) in original solution might carry higher charges, the charge decrease of hydroxyl Al species should have happened in mass spectrometer. Perhaps, Al species with tri-charge were more likely to be transformed from species in original solution because of the more slight difference in charges with the species in original solutions. Certainly, some other factors (e.g., molecular structure) might also affect the distribution of species with the above three kinds of charges.

In Fig. 2, each group of Al species have several dominant species, e.g., Al_1^+, Al_2^+, Al_3^+, and Al_4^+ in the group with mono-charge, Al_{13}^{2+} and Al_{16}^{2+} in the group with di-charge, Al_{13}^{3+} and Al_{16}^{3+} in the group with tri-charge. These species comprised the main component of these samples. Besides the dominant species mentioned above, some other categories of Al species with relative low content were also observed in Fig. 2. The phenomena can also be easily obtained from the distribution characteristics of Gaussian-shaped clusters in Fig. 1. On the whole, the quantification results in Fig. 2 were in good agreement with the peak distributions in Fig. 1, which might prove the feasibility of the quantification analysis method suggested in Section 3.1.

It can be seen from Fig. 1 that basicity (OH/Al ratio) of samples also has great effect on the distribution of Al species. Low-polymers (e.g., Al_1^+ at *m/z* 97 ± 18, Al_2^+ at *m/z* 157 ± 18, Al_3^+ at *m/z* 217 ± 18,

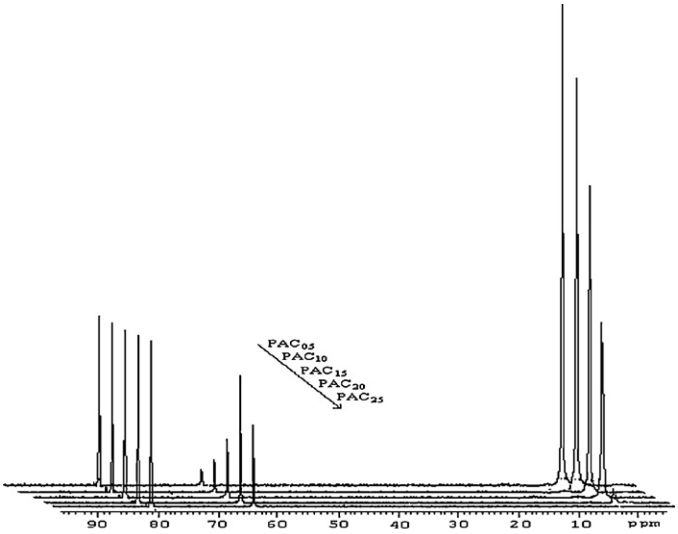

Fig. 3. ^{27}Al NMR spectra of polymeric Al solutions with different basicity (PAC_{05}, PAC_{10}, PAC_{15}, PAC_{20}, and PAC_{25}).

and Al_4^+ at m/z 313 ± 18) were mainly observed in the samples with low basicity (e.g., PAC_{05}, PAC_{10}). As for the mid-polymers (e.g., Al_{13}^+ at m/z 709 ± 18, Al_{13}^{2+} at m/z 337 ± 9, Al_{13}^{3+} at m/z 219 ± 6, Al_{16}^+ at m/z 835 ± 18, Al_{16}^{2+}at m/z 418 ± 9, and Al_{16}^{3+} at m/z 291 ± 6, respectively), they have been observed in all the samples and the contents increase obviously with the increase of basicity. This can be easily explained by the synthesis process of these samples. The addition of base into Al solution promotes the polymerization of monomers and low polymers in solution. With the increase of basicity, the contents of monomers and low-polymers all gradually decreased. However, the contents of mid-and high-polymers changed in opposite manner.

Fig. 3 shows the speciation results of polymeric Al solutions in ^{27}Al NMR spectroscopy. Similar with the speciation results of mass spectrometry, only a certain number of species, i.e., monomer (at 0 ppm), dimer (at 2–3 ppm) and Keggin-Al_{13}^{7+} (at 62.5 ppm) were detected on the spectra of these samples with ^{27}Al NMR spectroscopy. Since the integrated area of each peak in spectra is related to the relative abundance of that species, it can also be seen from Fig. 3 that the changes in the content of these species with basicity agreed with those in mass spectrometry. Monomers and dimers constituted the main species in the samples with low basicity. Mid-polymers (i.e., Keggin-Al_{13}^{7+}) gradually became the dominant species in samples with higher basicity. On the whole, the quantification results obtained with mass spectrometry agreed roughly with those in ^{27}Al NMR spectroscopy. The phenomena might also prove that mass spectrometry can be applied in the study of Al speciation.

3.3. *Classification of Al species identified from mass spectra*

Generally, three categories of Al species (i.e., monomer, mid-polymer and high-polymer or colloidal species) were often observed with ^{27}Al NMR spectroscopy (denoted as Al_m, Al_{13} and Al_{un}, respectively) and Ferron colorimetric method (denoted as Al_a, Al_b and Al_c, respectively). Previous studies have proved the feasibility and the consistency of the two methods [5,19]. For mass spectrometry, more categories of species with polymerization degree ranged from 1 to 31 have been observed in Fig. 2. Thus, to increase the comparability of Al speciation results in mass spectrometry with those obtained via the above two traditional methods, Al species obtained with mass spectrometry might also be classified into three categories.

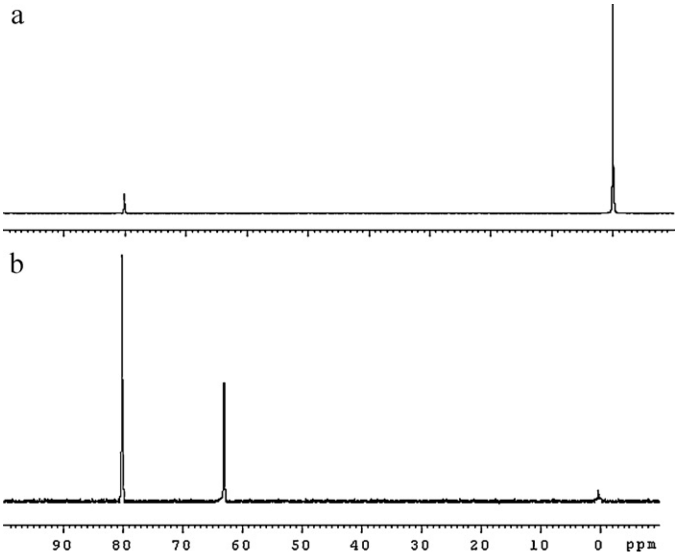

Fig. 4. ^{27}Al NMR spectra of monomeric Al solution (a) and purified Al_{13} solution (b).

Fig. 4a shows the speciation result of mononuclear Al solution (PAC_0) in ^{27}Al NMR spectroscopy. Only one category of Al species (i.e., monomer) has been detected in the solution. However, more categories of Al species with relative high content have also been observed with mass spectrometry in Fig. 5. Moreover, most of the species detected with mass spectrometry have low polymerization degree. Thus it can be drawn that most of the monomers in original solution have undergone polymerization reactions and were detected as low polymers in mass spectrometry [14,16].

In Fig. 6a, the total content of Al species with polymerization degree ranged from 1 to 10 in PAC_0 agreed roughly with that of the Al_a species in Ferron colorimetric method, and the Al_m species in ^{27}Al NMR spectroscopy. The slight difference was mainly ascribed to the polymerization of monomers in mass spectrometer and in spectrophotometer [19]. This can be further proved by the mid-polymer distributions in Fig. 6a. Mid-polymers have been detected in PAC_0 with mass spectrometry and Ferron colorimetric method, but are not observed with ^{27}Al NMR spectroscopy. On the whole, most of the low polymers in mass spectrometry have transformed from monomers in original solution and can be classified as the first categories as the Al_m species in ^{27}Al NMR spectroscopy and the Al_a species in Ferron colorimetric method, respectively.

As calculated form Fig. 4b, over 95% of species in purified Al_{13} solution (PAl_{13}) was Keggin-Al_{13}^{7+} in ^{27}Al NMR spectroscopy. However, only a certain number of main species with mid polymerization degree (i.e., Al_{19}^{3+}, Al_{20}^{3+}, $Al_{13}^{3+}$and Al_{16}^{n+}, $n = 1, 2, 3$) were detected with mass spectrometry in Fig. 5. Thus, it might indicate that Keggin-Al_{13}^{7+} also have undergone polymerization reactions in mass spectrometer. In Fig. 5, the total content of the Al_{13} species with three kinds of positive charges (i.e., Al_{13}^+, Al_{13}^{2+} and Al_{13}^{3+}) was only about 55% of that of the whole species in PAl_{13}. In fact, besides the Al_{13} species, the other three categories of mid-polymers (i.e., Al_{19}^{3+}, Al_{20}^{3+}, and Al_{16}^{n+}, $n = 1, 2, 3$) all have relative high content. Since most of species in original PAl_{13} solution was mainly composed of Keggin-Al_{13}^{7+}, these mid-polymers might have been transformed from the Keggin-Al_{13}^{7+} species in original solutions in mass spectrometer. The total content of these polymers constituted about 93 percent of that of the whole species in PAl_{13}, which agreed well with the speciation results of ^{27}Al NMR spectroscopy and Ferron colorimetric method (as shown in Fig. 6b). Therefore, Keggin-Al_{13}^{7+} in ^{27}Al NMR spectroscopy was mainly detected as these polymers in mass spectrometry. These mid polymers in mass spectrometry could be classified as the second category as the Al_{13}

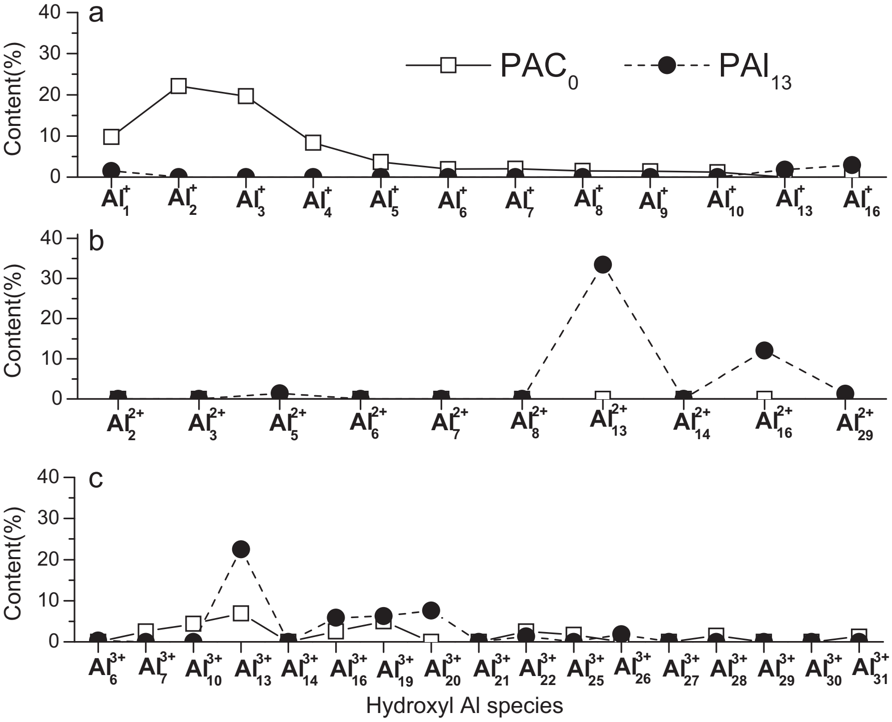

Fig. 5. Quantification analysis results of Al species with one (a), two (b) and three charges (c) in monomeric Al solution (PAC$_0$) and purified Al$_{13}$ solution (PAl$_{13}$) with ESI-TOF mass spectrometry.

species in ^{27}Al NMR spectroscopy and the Al$_b$ species in Ferron colorimetric method, respectively.

Besides the above mentioned species, some other species with relative low content (e.g., Al$_{26}^{3+}$, Al$_{28}^{3+}$) in PAC$_0$ and PAl$_{13}$ have also been observed with mass spectrometry. These species have higher polymerization degree (over 21) and might react with Ferron reagent very slowly or even have no reaction with Ferron. Additionally, these species cannot be observed with ^{27}Al NMR spectroscopy, but can be observed more easily in mass spectrometry. The reason can be described as follows: the soft ion modes of mass spectrometry changes the ligands and charges of these species in mass analyzer [9]. The ionized structures can be more easily detected with mass spectrometry. As shown in Fig. 6a, the speciation result of these species in mass spectrometry also agreed roughly with those in the other two traditional methods. Therefore, these high-polymers in mass spectrometry might be detected as the undetectable species (Al$_{un}$) in ^{27}Al NMR spectroscopy and the Al$_c$ species in Ferron colorimetric method.

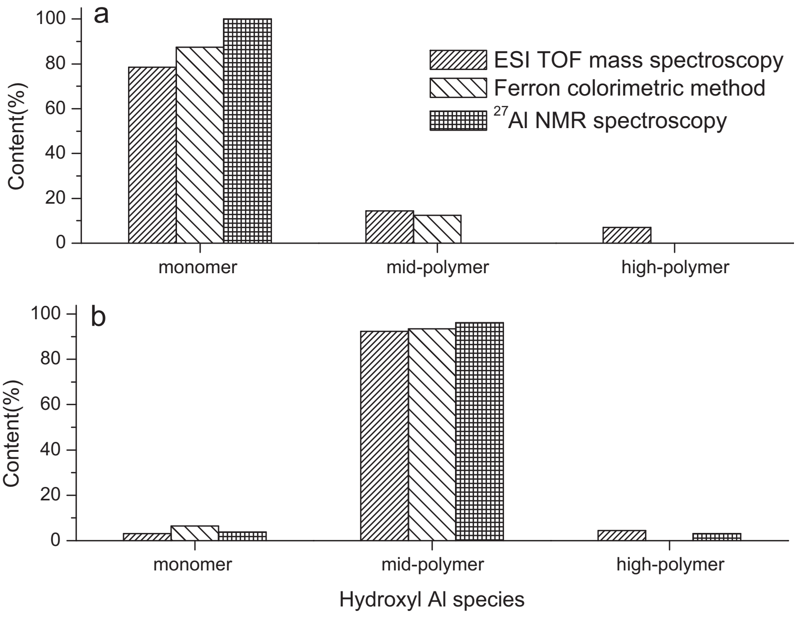

Fig. 6. Comparisons of speciation results of monomeric Al solution (a) and purified Al$_{13}$ solution (b) in ESI TOF mass spectrometry, Ferron colorimetric method, and ^{27}Al NMR spectroscopy.

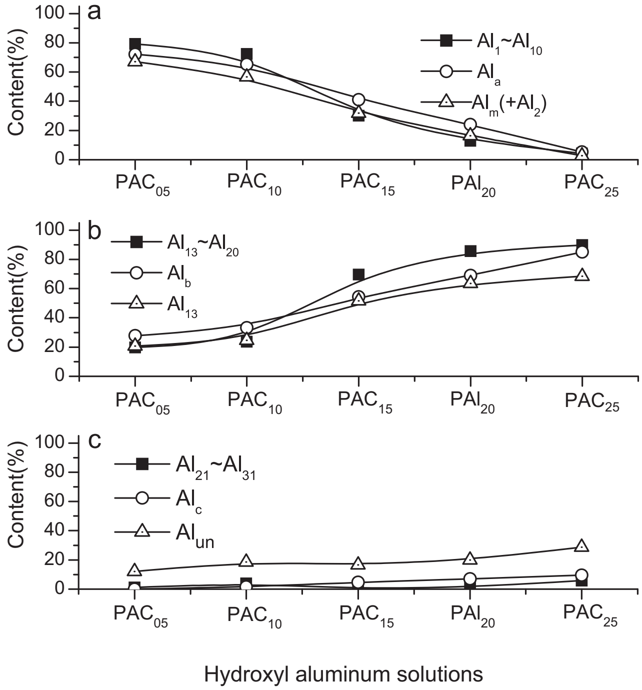

Fig. 7. Speciation results of polymeric Al solutions with different basicity in ESI TOF mass spectrometry (■), Ferron colorimetric method (○), and ^{27}Al NMR spectroscopy (△).

Therefore, three categories of species (i.e., Al_1–Al_{10}, Al_{13}–Al_{20}, and Al_{21}–Al_{31}) in mass spectrometry could be suggested as monomers, mid- and high-polymers, respectively. Since the classification pattern was put forward on base of the quantification analysis results of mononuclear Al solution and the purified Al_{13} solution, the feasibility of the classification pattern still needs further identification.

3.4. *Quantification analysis results of mass spectrometry*

Fig. 7 shows the quantification analysis results of polymeric Al samples in mass spectrometry, ^{27}Al NMR spectroscopy, and Ferron colorimetric method. On the whole, there exists a good agreement between the Al speciation results obtained by the above three spectrum methods. The content of monomers decreased with the increase of basicity, while the content of mid-polymers in samples increased obviously. As for the third category of species, no significant increase with basicity could be observed.

It can be drawn from Fig. 7a and b that the contents of monomers and mid-polymers obtained with Ferron colorimetric method are all higher than those obtained by ^{27}Al NMR spectroscopy. Since no hydrolysis and polymerization of Al species happened in ^{27}Al NMR spectrometer, the speciation results in ^{27}Al NMR spectroscopy often represent the original status of hydroxyl Al species in solutions. Thus, besides the monomers and Keggin-$Al_{13}{}^{7+}$ in ^{27}Al NMR spectroscopy, some other Al species might also coexist in solutions. Perhaps, these species could not be observed and were often considered as the undetected species (Al_{un}) in NMR spectroscopy.

Although there is still lack of direct evidence to prove the existence of these species [24,25], ESI TOF mass spectrometry might be a novel and feasible method to identify these species. In Fig. 2, besides mononuclear Al species ($Al_1{}^+$), some other low-polymers (e.g., Al_2–Al_5) were also detected in the samples with low basicity in mass spectrometry. As indicated in Fig. 6a, these low-polymers detected in the samples with low basicity were mainly transformed from monomers in original solution. However, the total content of these species (i.e., Al_1–Al_{10}) was obviously larger than the content of monomers (Al_m) in ^{27}Al NMR spectroscopy in Fig. 7a. Thus, the big difference is mainly ascribed to the existence of low polymers (e.g., Al_2–Al_{10}) in original solution. Part of these species with lower polymerization degree could react with Ferron quickly and were classified as the Al_a species in Ferron colorimetric method. Perhaps, the other species with higher polymerization degree often react with Ferron slowly and are classified as the Al_b species.

With the increase of basicity, these low-polymers in original solutions have been gradually transformed into high polymers (e.g., Keggin-$Al_{13}{}^{7+}$) and even cannot be detected in the samples with high basicity (e.g., 1.5, 2.0, 2.5). Therefore, low polymers (i.e., Al_1–Al_{10}) detected in PAC_{15}, PAC_{20} and PAC_{25} with mass spectrometry were mainly formed by the polymerization of monomers in original solution in mass spectrometer. The content of these low-polymers in mass spectrometry were in good agreement with those in ^{27}Al NMR spectroscopy in these samples.

As for the samples with high basicity, the total content of mid-polymers (i.e., Al_{13}–Al_{20}) in mass spectrometry were all higher than the content of mid-polymers (i.e., Keggin-$Al_{13}{}^{7+}$) in ^{27}Al NMR spectroscopy. Perhaps, some low-polymers have polymerized with Keggin-$Al_{13}{}^{7+}$ to form hydroxyl Al complex with higher polymerization degree (e.g., Al_{16}, Al_{19} and Al_{20}) in mass spectrometer and thus resulted in the bigger difference in the content of mid-polymers between the two methods. In fact, it can be seen from Fig. 7b that the Al_b content obtained by Ferron colorimetric method was also higher than the Keggin-$Al_{13}{}^{7+}$ content for every sample. This may further indicated that some mid-polymers, besides Keggin-$Al_{13}{}^{7+}$, exist in the solutions. Perhaps, these mid-polymers were also composed of $Al_{19}{}^{3+}$, $Al_{20}{}^{3+}$ and $Al_{16}{}^{n+}$, $n = 1, 2, 3$. This can be inferred from the fact that no other mid-polymers with high intensity have been observed in the mass spectra of these samples. Thus, the existence of these mid-polymers in original solutions also accounts for the big difference in the content of mid-polymers between Ferron colorimetric method and ^{27}Al NMR spectroscopy.

Besides the above mentioned species, high-polymers were also observed in all of the samples with the above three spectrum methods (Fig. 7c). However, the Al_{un} content in ^{27}Al NMR spectroscopy were obviously higher than the Al_c content in Ferron colorimetric method and the Al_{21}–Al_{30} content in mass spectrometry. The difference should be mainly ascribed to the existence of the above mentioned low- and mid-polymers which cannot be observed with ^{27}Al NMR spectroscopy but can be detected with the other two methods. It can also be inferred from Fig. 7c that the Al_c species were mainly composed of hydroxyl Al complex with polymerization degree ranged from 21 to 31. The reason is that the Al_c content in Ferron colorimetric method agrees well with the Al_{21}–Al_{30} content in mass spectrometry in the samples with different basicity. On the whole, the quantification results of mass spectrometry agree better with those of Ferron colorimetric method.

4. Conclusions

The speciation results of ESI-TOF mass spectrometry were in accord with those of Ferron colorimetric method and ^{27}Al NMR spectroscopy. Quantification analysis method of mass spectrometry was proved to be feasible. The above three spectrum methods all have its specialty and can provide additional explanation for each other. Minor differences in Al speciation results still existed between the above three methods. Much more factors (e.g., polymerization degree of Al species, application conditions of mass spectrometer) should be further considered to optimize the quantification analysis method of mass spectrometry.

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