Differentiation of hydroxyl-aluminum species at lower OH/Al ratios by combination of ^{27}Al NMR and Ferron assay improved with kinetic resolution

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Abstract

The hydroxyl-Al polymers are the most effective components in PACl coagulants, but their chemical speciation is often indistinct especially at lower molar OH/Al ratios (B). Two sets of hydroxyl-Al solutions with different B values and preparation temperatures were studied with both Ferron assay and ^{27}Al NMR spectroscopy. By using the modified kinetic resolution procedure to fit the scanning absorbance data, the reactive polymeric Al species (Al_b) could be differentiated further into two fractions: the faster reacting polymers Al_{b1} and slower reacting polymers Al_{b2} . They were distinguished by their distinct rate constants of reactions with Ferron. It was identified simultaneously by the ^{27}Al NMR spectroscopy that the Al_{b2} fraction closely corresponded to Al_{13} of Keggin-structure in most samples, while the Al_{b1} at the moderate OH/Al ratios of $B < 2$ would be assigned to the species of Al_6 -type series which were undetectable in current ^{27}Al NMR spectrum (Al_{un}). Conventional ^{27}Al NMR spectroscopy in combination with Ferron assay improved with kinetic resolution can better explore the chemical speciation for hydroxyl-Al polymers in partially neutralized Al solutions and thus give a better explanation of coagulation mechanisms of these species when they were applied in water treatment. © 2007 Elsevier B.V. All rights reserved.

Keywords: Al_{13} ; Reactive Al polymers; Speciation; Al-Ferron reaction kinetics

1. Introduction

Alum and PACl have been widely applied as coagulants in water and wastewater treatment. Their hydroxyl-aluminum polymers were recognized as the most effective components in Al coagulants [1–3]. A thorough understanding of the nature and properties of the hydrolyzed-Al species in partially neutralized solutions should be of great help in the understanding of coagulation mechanisms and the improvement of inorganic polymer flocculants. Many chemical and instrumental methods have been adopted to characterize and quantify Al species in solutions. ^{27}Al NMR spectroscopy and Ferron assay are the two most commonly used methods, but none of them can set forth a perfect pattern yet.

The ^{27}Al NMR spectroscopy has been widely recognized as the sole instrumental method to identify the Al species directly

[4–6]. However, it can determine only a few Al species like mononuclear (Al_m), oligomers (Al_2 even Al_3), and tridecamer (Al_{13}). It can identify currently neither the octahedral coordinated lower polymers as $\text{Al}(\text{O})_6$ series, nor the polymers higher than Al_{13} except the recently revealed Al_{30} produced at elevated temperature [7–9]. All of these species can only be referred to the undetectable Al species (Al_{un}) in ^{27}Al NMR spectroscopy.

On the basis of the kinetic difference in reactions of Ferron with various Al species, Ferron assay has been employed to distinguish mononuclear (Al_a), reactive polymers (Al_b) and inert high polymers or colloidal Al species (Al_c) in hydroxyl-Al solutions [10,11]. Although covering the whole space of Al content, it can give only a rough classification without any actual species in each category. For the more accurate speciation of these Al species, pseudo-first-order reactions and nonlinear regression methods have also been utilized to distinguish the hydroxyl- Al_b by Zelazny and other authors [12–15]. However, their focus of attention emphasized mostly on the distinguishing of inert fraction from Al_{13} at higher OH/Al ratio and the identification by ^{27}Al NMR has never been completed. A few authors assumed

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that besides Al_{13} some other lower polymers may exist in the Al_b species but none of them has proved the speculation so far [16–18].

The correspondence between the results of ^{27}Al NMR spectroscopy and Ferron assay has been studied by Parker and Bertsch [19,20]. They demonstrated that the Al_b in Ferron assay was identical with Al_{13} in NMR spectroscopy. However, this finding may only apply to the samples dominated by Al_{13} at higher OH/Al ratios, but not apply to the samples with moderate OH/Al ratios and abundant Al_{un} species.

Previously, the traditional six-member-ring hexamer structure model of hydroxyl-aluminum species was strongly challenged by the Keggin-structure model that has been verified with ^{27}Al NMR technique. However, benefiting from the advanced instrumentation the situation is subject to change. Singhal and Keefer [7] by small angle X-ray scattering and Pophristic et al. [21] by molecular dynamics demonstrated the existence of the six-member-ring hexamer species in the hydroxyl-Al solution. Moreover, Seichter et al. [22] reported that some crystal solid of $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]\text{Cl}_{15} \cdot 13\text{H}_2\text{O}$ has been prepared successfully and identified by XRD. Allouche et al. [23] reexamined it later with 2D ^{27}Al 3QMAS NMR and referred to polycation as Mögel- Al_{13}^{15+} . Its structure presented as the pure six-member-ring Al_{13} with an $\text{Al}(\text{O})_6$ in the center instead of the octahedral structure $\text{Al}(\text{O})_4$ in Keggin- Al_{13} . It was reviewed also by Casey (2004) with the term of *flat*- Al_{13} $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_6]^{15+}$ and assumed the existence of another polycation $[\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{13}]^{10+}$ species. These hydroxyl-Al polymers can all be attributed to Al_6 series.

The aim of this paper is to study the hydroxyl-aluminum solutions at the moderate OH/Al ratio by Ferron assay with kinetic resolution to classify the reactive polymers Al_b into Al_{b1} and Al_{b2} and for the first time assigned and demonstrated them by ^{27}Al NMR spectroscopy to Al_6 series and Al_{13} , respectively. This combination of methods provides a better approach to identify hydroxyl-aluminum species in partially neutralized aluminum solution and thus be helpful to clarify the coagulation mechanism in water treatment processes.

2. Materials and methods

2.1. Preparation of hydroxyl-Al solution

In this study, deionized water was used to prepare all the solutions and all the reagents were of analytical grade chemicals. Hydroxyl-Al solutions were freshly prepared by using the micro-titrating method [25]. Under rapid stirring and bubbling with nitrogen gas, a calculated volume of 0.27 mol L^{-1} AlCl_3 solutions was titrated slowly with 0.5 mol L^{-1} 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) that were chosen as 0.5, 1.0, 1.5, 2.0 and 2.5 in this study. Two sets of hydroxyl-Al solutions were prepared at 25 ± 0.1 and 80 ± 0.1 °C. The final concentration of total Al (Al_T) in every sample was adjusted to about 0.1 mol L^{-1} with deionized water. Their exact concentrations were measured with ICP-OES (Perkin-Elmer Co. U.S.A.).

The samples were aged for 24 h at room temperature and their final pH values were measured with MP220 pH meter (Mettler Toledo, Switzerland) before being preserved at 4 °C for analysis.

2.2. ^{27}Al NMR spectroscopy

The two sets of hydroxyl-Al solutions were examined with a 500 MHz ^{27}Al NMR (Brookhaven Co., U.S.A). The instrumental settings and experimental conditions were: NS = 128, P1 = 20 μs , PL1 = −3 dB. Solvent: D_2O , and $T = 298 \text{ K}$. The inner standard was 0.05 mol L^{-1} $\text{Al}(\text{OD})_4^-$ solution and its chemical shift is 80 ppm. The signals near 0, 3–4 and 62.5 ppm represent mononuclear Al (Al_m), dimeric Al (Al_2) and the tetrahedral $\text{Al}(\text{O})_4$ core (and 1/13 content) of Al_{13} $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, respectively. The concentration of each species was determined by the ratio of the integrated intensity of its corresponding peak to that of $\text{Al}(\text{OD})_4^-$ at 80 ppm. The Al_{13} content was calculated by multiplying the $\text{Al}(\text{O})_4$ concentration by 13. 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 solution [17,18].

2.3. Kinetic interaction of Ferron with hydroxyl-Al solution

The detailed procedures for the preparation of Ferron colorimetric solution can be found in Wang et al. [26]. The 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. 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 [18,19,26]. 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 $\text{Al}_a + \text{Al}_b$ and that of Al_T in solutions.

3. Results and discussion

3.1. Chemical speciation of hydroxyl-aluminum with kinetic resolution

According to the assumption that various Al species have different reaction durations with Ferron, three categories of Al species, mononuclear (Al_a), reactive polynuclear (Al_b) and inert high polymers (Al_c), can often be distinguished with the Ferron assay (as shown in Fig. 1). Generally, when no detectable absorbance increase can be observed, the reaction of ($\text{Al}_a + \text{Al}_b$)

Fig. 1. Schematic diagram of the reaction kinetics of hydroxyl-Al species with Ferron colorimetric reagent. (I) and (II) represent the early and later phases of the Al_b -Ferron reaction, respectively. The triangle curve refers to the Ferron reaction with hydroxyl-Al species; the solid and dot-dashed curves refer to the absorbance development of Al_{b1} -Ferron and Al_{b2} -Ferron reactions with time, respectively. The vertical dashed line represents the boundary between (I) and (II).

with Ferron is supposed to have reached the end point and the total reactive Al ($\text{Al}_a + \text{Al}_b$) content can then be quantified from the absorbance with an appropriate standard curve [11,18]. However, no consensus has yet been reached on the duration proposed operationally for the Al_a reaction, and thus the content of Al_b cannot be accurately determined too [27]. Even the duration was well determined, employing a constant operationally defined cutoff may be erroneous because the duration of mononuclear Al interactions with Ferron depends much on the B value (OH/Al molar ratio) [13,19]. Thus, computational approach based on the Al-Ferron kinetics, instead of empirical determination of Al-Ferron reaction durations, may be a preferred method for Al speciation.

After being mixed with Ferron colorimetric solution, the mononuclear Al species in samples react with Ferron instantaneously and the oligomers as dimer or trimer also react with fast rates. However, as far as the higher polymeric Al species are concerned, the condition would be more complex. There are

many different bi-hydroxyl- $(2\mu_2\text{-OH})$ and oxy- $(\mu_4\text{-O})$ bridges bonding the Al atoms in their structures. Ferron will compete with hydroxyl- and later more difficultly with oxy-bonds before the bridges break down to form the Al-Ferron coloring species [13,28]. Thus, the rate-limiting step of Ferron interaction with hydroxyl-Al solution is the degradation of polymers and different forms of Al species often react at varying rates with Ferron. Fig. 1 shows the schematic diagram of the reaction kinetics of Ferron with hydroxyl-Al species. The continuous absorbance versus time function (i.e., the triangle curve) reveals an initial rapid absorbance increase that becomes slow at longer time. Since most mononuclear Al reacts with Ferron instantaneously, the absorbance increase observed from the triangle curve is mainly ascribed to the Ferron interactions with reactive hydroxyl-Al polymers (Al_b) in the sample. Thus, based on the Al_b -Ferron reaction kinetics, a pseudo-first-order reaction has often been applied to differentiate the Al_a and Al_b in samples [19]. The rate expression is

$$\log[\text{Al}_b]_{\text{un}} = \log[\text{Al}_b] - \left(\frac{k_b}{2.303} \right) t \quad (1)$$

where $[\text{Al}_b]_{\text{un}}$ is the concentration of the unreacted Al_b at any time. The initial concentration of Al_b (i.e., $[\text{Al}_b]$ in Eq. (1)) in a certain sample can then be calculated by extrapolating a linear segment of an appropriate plot of the Al_b -Ferron reaction back to time $t=0$, with k_b calculable from the slope of the same plot. On basis of the estimate result of Al_b , the concentration of Al_a in every sample can be obtained by the difference of the Al_b fraction with the total reactive Al content ($\text{Al}_a + \text{Al}_b$). The speciation results of Al_a and Al_b are listed in Table 1.

As can be seen from Fig. 1, based on the slope change of the Δ curve, Al_b can be divided into two categories of Al species, i.e., faster reacting and slower reacting polymers (denoted as Al_{b1} and Al_{b2} , respectively). Only after the majority of Al_{b1} completed their interactions with Ferron, slower reacting Al polymers (Al_{b2}) started to become the main species to react with Ferron in the later phase (II). The solid curve is supposed to be the absorbance development of Al_{b1} -Ferron complex with time. The dotted curve which represents the absorbance development

Table 1
Speciation of samples with the preparation temperature of (a) 25 and (b) 80 °C by Al-Ferron reaction kinetics

B	pH	Al_T (M)	$\text{Al}_a\%$	$\text{Al}_b\%$	$\text{Al}_c\%$	k_{b1}	k_{b2}	$\text{Al}_{b1}\%$	$\text{Al}_{b2}\%$	R^2
Samples (a)										
0.5	3.84	0.1069	62.68	36.28	1.04	0.01916	0.00061	21.51	14.77	0.9972
1.0	3.92	0.1184	49.37	49.64	0.99	0.01906	0.00073	16.41	33.23	0.9986
1.5	4.00	0.1168	33.42	61.57	5.01	0.02201	0.00071	3.20	58.37	0.9998
2.0	4.16	0.1068	13.58	81.72	4.70	0.02816	0.00077	0.31	81.41	0.9998
2.5	5.37	0.1088	1.84	62.84	35.32	0.01943	0.00066	0.15	62.69	0.9877
Samples (b)										
0.5	3.66	0.1203	72.21	30.32	^a —	0.02199	0.00139	14.91	15.41	0.9658
1.0	3.71	0.1206	56.23	41.07	2.70	0.01272	0.00166	8.83	32.24	0.9900
1.5	3.78	0.1186	41.05	53.75	5.19	0.02099	0.00152	5.26	48.49	0.9970
2.0	3.87	0.1188	23.98	67.72	8.30	0.01931	0.00154	1.08	66.64	0.9974
2.5	4.12	0.1232	5.37	81.62	13.01	0.02001	0.00154	0.59	81.02	0.9967

^a Undetectable.

Fig. 2. Reaction kinetics of Ferron with reactive hydroxyl-Al polymers in the two sets of samples with different B values and different preparation temperatures (a) 25 and (b) 80 °C.

of the Al_{b2} fraction is obtained by subtracting the contribution of Al_{b1} fraction from the overall absorbance–time curve. After the completion of Al_a -Ferron reaction, the above two categories of Al species (Al_{b1} and Al_{b2}) begin to react with Ferron and result in an irreversible bimolecular reaction. With the nonlinear least-squares analysis, the Al_b -Ferron kinetic reaction can be fitted with Eq. (2) to quantify Al_{b1} and Al_{b2} :

$$A = A_0 + A_1(1 - \exp(-k_{b1}t)) + (A_2 - A_1)(1 - \exp(-k_{b2}t)) \quad (2)$$

where A and A_0 is the absorbance measured at any time and at time equal to zero, respectively, t the reaction time (s), A_1 and A_2 the absorbance of the complex of Ferron with Al_{b1} and Al_b , respectively, and k_{b1} and k_{b2} are the first-order rate constants for the Al_{b1} and Al_{b2} , respectively.

Assigning $A_2 = A_\infty - A_0$, Eq. (2) can be transformed into the following one:

$$A = A_\infty - A_1 \exp(-k_{b1}t) - (A_\infty - A_0 - A_1) \exp(-k_{b2}t) \quad (3)$$

where A_∞ is the absorbance measured at infinite time (e.g., 7200 s). Thus, A_∞ and A_0 are two constants in Eq. (3) and the number of parameters to be fitted decreases to three (i.e., A_1 , k_{b1} and k_{b2}).

For the Ferron assay of every sample of hydroxyl-Al solution, a plot of absorbance against time was fitted with Eq. (3) by using a nonlinear least-square inversion technique with OriginPro 7.5 software at 95% confidence. The absorbance of mononuclear Al in each solution was calculated from the Al_a concentration with a standard curve. Then, with A_0 designated as a constant for every test sample, the fitted results of the reaction kinetics of Ferron with reactive hydroxyl-Al polymers for the two sets of samples (a and b) are summarized in Table 1 and also plotted in Fig. 2.

The kinetic reactions of Ferron with reactive polymeric Al in the two sets of hydroxyl-Al solutions were well described by Eq. (3) (Fig. 2) with $R^2 \geq 0.96$ for all samples (Table 1). Generally, upon increasing the B value, a strong decrease in the faster reacting Al polymers (Al_{b1}) was accompanied by an increase in the slower reacting Al species (Al_{b2}). In the early phase (I) of the Al_b -Ferron reaction, the model fitted k_{b1} was mainly attributed to the Ferron interaction with Al_{b1} . As the reaction proceeds, the fraction of faster reacting aluminum (Al_{b1}) continuously decreased and the slower reacting aluminum (Al_{b2}) became predominant, so the model fitted k_{b2} mainly represented the Al_{b2} reaction in the later phase (II) (Fig. 1 and Table 1). Since the difference between k_{b1} and k_{b2} is over one order of magnitude in general, the separation of hydroxyl-aluminum species into two groups is rationalized.

3.2. Correspondence between Ferron assay and NMR spectroscopy

Fig. 3 shows the ^{27}Al NMR spectroscopy result of different hydroxyl-Al solutions studied. The speciation results of the two sets of hydroxyl-Al solutions with NMR spectroscopy are shown in Table 2, together with the Ferron assay results for the purpose of comparison.

The fractions of Al_{13} determined by NMR spectroscopy and Al_b in Ferron assay are both developing synchronously with the increase of B value (OH/Al molar ratio) and generally reach their maxima at high B value (Table 2 and Fig. 3). The exceptional decrease of the sample at 25 °C and $B = 2.5$ is due to the partial transformation of some species into the inert Al_c . It is evident through comparison that there is certain discrepancy in the relative abundance (%) between the Al_{13} and Al_b fractions. The Al_b fractions are all greater than those of Al_{13} but the difference decreases at higher B values. Therefore, some

Fig. 3. ^{27}Al NMR spectrum of hydroxyl-Al solutions with different B values (0.5, 1.0, 1.5, 2.0 and 2.5) and various preparation temperatures (a) 25 and (b) 80 °C.

other Al species besides Al_{13} polymers must co-exist as reactive hydroxyl-Al polymers. These species cannot be detected by current NMR spectroscopy but can react with Ferron. Moreover, the experimental results also indicate that the Al_{13} fraction may be much closer to the content of $\text{Al}_{\text{b}2}$ and even Al_{b} in the range of $B=1.5$ –2.0. The latter condition has been demonstrated by Parker and Bertsch [19,20].

3.3. Assigning the hydroxyl-aluminum species of $\text{Al}_{\text{b}2}$

For all the samples, model fitted rate constants $k_{\text{b}2}$ of $\text{Al}_{\text{b}2}$ reacting with Ferron are close approximate to each other over the range of B values investigated (Table 1), implying that slower reacting Al species ($\text{Al}_{\text{b}2}$) may be of a single form [13]. Fig. 4 shows the comparison of Al_{13} with $\text{Al}_{\text{b}2}$ in hydroxyl-Al solutions with different B values. It is noteworthy that the amounts of $\text{Al}_{\text{b}2}$ estimated by the Al-Ferron reaction kinetics correspond closely to those of Al_{13} polymers determined with direct NMR measure-

Fig. 4. Distributions of Al_{13} and $\text{Al}_{\text{b}2}$ in two sets of hydroxyl-Al solutions with different preparation temperatures (a) 25 and (b) 80 °C.

Table 2
Speciation of hydroxyl-Al solutions prepared at (a) 25 and (b) 80 °C with ^{27}Al NMR spectroscopy and Ferron assay

B	pH	Al_{T} (M)	$\text{Al}_{\text{m}}\%$	$\text{Al}_{\text{2}}\%$	$\text{Al}_{13}\%$	$\text{Al}_{\text{un}}\%$	$\text{Al}_{\text{a}}\%$	$\text{Al}_{\text{b}}\%$	$\text{Al}_{\text{b}1}\%$	$\text{Al}_{\text{b}2}\%$	$\text{Al}_{\text{C}}\%$
Samples (a)											
0.5	3.84	0.1069	53.35	4.34	24.37	17.94	62.68	36.28	21.51	14.77	1.04
1.0	3.92	0.1184	37.69	2.75	36.39	23.17	49.37	49.64	16.41	33.23	0.99
1.5	4.00	0.1168	26.3	2.28	56.79	14.63	33.42	61.57	3.20	58.37	5.01
2.0	4.16	0.1068	12.41	^a —	77.85	9.74	13.58	81.72	0.31	81.41	4.70
2.5	5.37	0.1088	—	—	43.19	56.81	1.84	62.84	0.15	62.69	35.32
Samples (b)											
0.5	3.66	0.1203	62.07	5.02	20.81	12.1	72.21	30.32	14.91	15.41	—
1.0	3.71	0.1206	43.26	3.52	34.66	18.56	56.23	41.07	8.83	32.24	2.70
1.5	3.78	0.1186	31.86	—	51.59	16.55	41.05	53.75	5.26	48.49	5.19
2.0	3.87	0.1188	16.51	—	63.47	20.02	23.98	67.72	1.08	66.64	8.30
2.5	4.12	0.1232	2.77	—	68.51	28.72	5.37	81.62	0.59	81.02	13.01

^a Undetectable.

ments, especially in those samples where B values ranged from 1.0 to 2.0. For the samples with higher B value (e.g., 2.5), the contents of $\text{Al}_{\text{b}2}$ are obviously higher than those of $\text{Al}_{\text{I}3}$ (Fig. 4). The extra amount may result from some polymeric Al species which has higher polymerization degree than $\text{Al}_{\text{I}3}$ (e.g., Al_{30}) or some accumulative aggregates. They may react with Ferron in monitoring period as long as 7200 s but cannot be detected with NMR spectroscopy. On the other hand, the contents of $\text{Al}_{\text{b}2}$ were slightly smaller than those of $\text{Al}_{\text{I}3}$ polymers in the samples with lower B value (e.g., 0.5). The extrapolating method may overestimate Al_{a} in a more acidic condition, thus underestimating Al_{b} and related $\text{Al}_{\text{b}2}$. Nevertheless, it can be demonstrated by the NMR method that the slower reacting Al polymers ($\text{Al}_{\text{b}2}$) is mainly composed of $\text{Al}_{\text{I}3}$ polycation with Keggin-structure. The chemical speciation results derived from the structural and kinetic analyses are consistent even at moderate OH/Al ratios.

3.4. Assigning the hydroxyl-aluminum species of $\text{Al}_{\text{b}1}$

By making kinetic resolution on the Ferron assay results, the hydroxyl-aluminum species have been rationally differentiated into $\text{Al}_{\text{b}1}$ and $\text{Al}_{\text{b}2}$. The $\text{Al}_{\text{b}2}$ species may be assigned to the $\text{Al}_{\text{I}3}$ with Keggin-structure as discussed above. The $\text{Al}_{\text{b}1}$ species may belong to the Al_6 -type series like six-member-ring structure with pure μ_2 -OH or μ_3 -OH linkages between Al atoms. This will be confirmed with the elucidation of the Al speciation results in the following two sections.

3.5. NMR undetectable aluminum species Al_{un}

Three categories of Al species, i.e., Al_{m} , Al_2 and $\text{Al}_{\text{I}3}$ can often be determined by the conventional ^{27}Al NMR spectroscopy. On the basis of mass conservation, all the residual undetectable species are summed as Al_{un} . Though the octahedrons around the core in Keggin- $\text{Al}_{\text{I}3}$ are also undistinguishable in the NMR spectrum, it is already deducted from the Al_{un} when quantifying $\text{Al}_{\text{I}3}$. The species distribution pattern in Table 1 shows that the contents of the oligomer Al_2 and the inert high polymers Al_{c} at $B < 2.0$ are almost negligible. Thus, the $\text{Al}_{\text{b}1}$ fractions should constitute the predominant component of the Al_{un} . The fractions of Al_{un} , Al_{c} and $\text{Al}_{\text{b}1}$ as a function of B are shown in Fig. 5. Al_{un} transforms gradually from $\text{Al}_{\text{b}1}$ to Al_{c} and other super high polymers in pace with the increasing B ratios. In addition, the polymerization degree of the Al_{un} at $B < 2$ must be no larger than that of Keggin- $\text{Al}_{\text{I}3}$ polycation.

3.6. The structural difference between Al_6 -type series and Keggin- $\text{Al}_{\text{I}3}$

Singhal and Keefer [7], Pophristic et al. [21] assigned Al_{un} formed at lower OH/Al ratios to the six-member-ring Al_6 ($\text{Al}_6(\text{OH})_{12}^{6+}$) species. Seichter et al. [22], Allouche et al. [23] reported the existence of Al_6 -type polycation [$\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_6^{15+}$] with μ_3 -OH bridges in the core. Casey [24] even assumed the existence of another Al_6 -type polycation [$\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{13}^{10+}$] species. Therefore, $\text{Al}_{\text{b}1}$ formed at moderate OH/Al ratios may belong to Al_6 -type series which

Fig. 5. Distributions of $\text{Al}_{\text{b}1}$, Al_{c} and Al_{un} in two sets of hydroxyl-Al solutions with different preparation temperatures (a) 25 and (b) 80 °C.

include various polymers and species with the structure of octahedrons arrayed similar to the six-member-ring style (μ_2 -OH, μ_3 -OH).

When the hydroxyl-Al solutions are mixed with Ferron colorimetric solution, the moderate polymers with $\text{Al}(\text{O})_6$ structure ($\text{Al}_{\text{b}1}$) may be subject to decomposition under the impact of Ferron, because the μ_2 -OH or μ_3 -OH bridges between the Al atoms in the structure are easy to break down to form colored Al-Ferron complex compound. However, as far as the Keggin- $\text{Al}_{\text{I}3}$ polymers ($\text{Al}_{\text{b}2}$) are concerned, it is more difficult for Ferron to compete with the hydroxyl bridges. The tetrahedral $\text{Al}(\text{O})_4$ core with μ_4 -O bonds in Keggin- $\text{Al}_{\text{I}3}$ polycation is stronger and inert to break down as indicated by Furrer et al. [29] and Casey et al. [30]. Therefore, the $\text{Al}_{\text{b}1}$ and $\text{Al}_{\text{b}2}$ species in the reactive Al_{b} fractions can be differentiated by their distinct kinetic rate constants in the reaction with Ferron. The reaction rates with Ferron for $\text{Al}_{\text{b}2}$ ($k_{\text{b}2}$, ca. 10^{-3} or 10^{-4} s^{-1}) are often much slower than those for $\text{Al}_{\text{b}1}$ ($k_{\text{b}1}$, ca. 10^{-2} s^{-1}) over one order of magnitude. Moreover, there is no significant change in $k_{\text{b}1}$ and $k_{\text{b}2}$ as the value of B increases, respectively. This may further indicate that the two categories of Al species (i.e., $\text{Al}_{\text{b}1}$ and $\text{Al}_{\text{b}2}$) have different individual chemical structure, polymerization degree and related kinetic factors.

In fact, the rate constants deduced from the model fitting calculations are only a statistical average for a certain group of polymers in solution, and they are often affected by reaction conditions, such as solution pH, Al concentration and some other unknown factors [14]. Therefore, a slight of change in the magnitude of $k_{\text{b}1}$ and even $k_{\text{b}2}$ is of no surprise. However, the Ferron assay with improved kinetic resolution and ^{27}Al NMR spectroscopy in combination can provide detailed information about Al speciation. Differentiating the reactive hydroxyl-Al polymers (Al_{b}) at the moderate OH/Al ratios into $\text{Al}_{\text{b}1}$ and $\text{Al}_{\text{b}2}$ and assigning the $\text{Al}_{\text{b}1}$ as species of Al_6 -type series will improve the knowledge about the composition and transformation model of aqueous aluminum. Moreover, the Ferron assay improved with kinetic resolution, instead of the ^{27}Al NMR spectroscopy,

can also be used to quantify Al_{13} in hydroxyl-Al solutions. This finding should be helpful for the wider applications of the Al_{13} polycation in petroleum, catalysis, pharmaceutical, ceramics water treatment and other industries.

Two categories of Al species (i.e., Al_6 -type series and Keggin- Al_{13}) might present in partially neutralized Al solutions. There often exist significant differences in molecular structure, charge and transformation model between them. As the effective components in water treatment, the two categories of Al species would show different coagulation mechanisms [11]. Thus, based on the speciation study of the Al salt flocculants with the methods mentioned above, the more detailed information on the coagulation mechanisms of various species can be more easily obtained. Moreover, the full understanding of their speciation would also encourage the innovation of high efficient water treatment process and the development of the inorganic polymer flocculants with high content of the most effective Al species.

4. Conclusions

For the most effective components in PACl coagulants, hydroxyl-Al polymers has been further differentiated into the faster reacting polymers Al_{b1} and slower reacting polymers Al_{b2} by their distinct rate constants of reactions with Ferron. The combined application of Ferron assay with NMR spectroscopy provides a better approach to study the molecular structure, transformation model and speciation of various Al species existed in flocculants. The speciation results of partially neutralized Al solutions would facilitate various Al complexes to achieve their optimal effectiveness in different industrial applications.

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