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Relationship between developer dosage and accurate determination of medium polymer species (Al_b) in Al-based flocculants

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ABSTRACT

Typical hydroxyl polyaluminum solutions (purified Keggin-Al_{13} and OH/Al = 0.5~2.3) were employed to study the influence of different developer dosage (Ferron, 7-iodo-8-hydroxyquinoline-5-sulfonicacid, [Ferron]) on the variation trend of absorbance-time (A-t) curves determined by Ferron timed spectrophotometry (Ferron assay) and exact determination of Al_b content ([Al_b]). On this basis, the difference existed between [Al_b] and Keggin-Al_{13} (K-Al_{13}) content ([$Al_{13,\ NMR}$], determined by ^{27}Al NMR) in the same solution was further inspected in the hydroxyl polyaluminum solutions (HPAs) with different OH/Al molar ratios. Results indicated that: (1) in chromogenic system, the optimal [Ferron] achieving accurate determination of [Al_b] is 2.0×10^{-3}~3.0×10^{-3} mol/L, where the total Al concentration ([Al_T]) is within 2.0×10^{-5}~8.0×10^{-5} mol/L. Insufficient [Ferron] will result in unreasonably low measuring results. (2) Significant difference exists between [Al_b] and [$Al_{13,\ NMR}$] in the same HPAs, and $\Delta Al_b = [Al_{13,\ NMR}]-[Al_b]>0$. This study lays a scientific foundation for right denotation of the content of effective Al species in HPAs, and clarifies the confusion existed in the speciation correlation between Al_b and K-Al_{13}.

Keywords: Ferron-timed spectrophotometry (Ferron assay); Hydroxyl polyaluminum solutions (HPAs); Al_b content ([Al_b]); Difference between Al_b and $Al_{13,NMR}$

1. Introduction

In the field of water treatment, polyaluminum chloride is one of the most commonly used inorganic polymer flocculants, and its performance is closely related with the species of hydroxyl polyaluminum distributed in it [1–5]. Al_b, medium polymer species defined by Ferron assay, is the optimal coagulation-flocculation ingredient, whose content can directly reflect the efficiency of polyaluminum chloride in coagulation process. Thus, high Al_b content is the major improvement target of the production technology of Al-based coagulants [6–9]. As a result, tailor researching HPA species and their pertinent properties has been the focus and cutting-edge topics of Al chemistry research [4,10,11]. Proper and effective analytical techniques will provide direct guidance for them.

Ferron timed spectrophotometry (Ferron assay) and ^{27}Al nuclear magnetic resonance (^{27}Al NMR) are two important analytical tools for the in-depth study on HPA species. Within the scope of their respective capacities, they all accelerated the development of aluminum water chemistry [12–14]. However, compared with ^{27}Al NMR method, Ferron assay has its significant advantages: High sensitivity. The measurement of Al species existed in environmental samples (~2×10^{-5} mol/L) can be achieved directly. The other is simple, low cost, no additional special equipment. Moreover, Ferron assay will become a standard identification method for the speciation and quantification of inorganic polymer flocculants [5]. Despite all of these, absence of uniform and stan-

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dardized operating procedure hinders the extensive use of Ferron assay [5,15–18]. Over the years, researchers have been tried to improve and optimize it. It has been found in this study that there are still some important issues should be further clarified for Ferron assay: (1) the influence of [Ferron] on accurate determination of [Al_b]. A-t curves determined in the HPA-Ferron chromogenic system will change with varied [Ferron], which further affects the calculation of [Al_b] inevitably. (2) the right relationship between [Al_b] and [$Al_{13,\ NMR}$] in the same HPAs has not been established, so the research conclusions are numerous and complicated. Various results, such as [Al_b]>[$Al_{13,\ NMR}$], [Al_b]=[$Al_{13,\ NMR}$] or [Al_b]<[$Al_{13,\ NMR}$], all had been reported [12,19–23].

Thus, the aims of this study are (1) to investigate the influence of different [Ferron] on the changing trend of A-t curves, and confirm [Ferron] is the key factor influencing accurate determination of [Al_b]. An appropriate colorimetric condition for the accurate determination of [Al_b] eventually proposed; (2) to analyze the error of [Al_b] measurement introduced by insufficient [Ferron]; (3) to further study the difference existed between [Al_b] and [$Al_{13,\ NMR}$] in the same HPAs under the improved determination conditions. The law of difference between [Al_b] and [$Al_{13,\ NMR}$] included in each HPAs was studied, and the objective reason for this discrepancy was confirmed for the first time, which will provide direct theoretical direction for the study of practical application of Al-based flocculants.

2. Materials and methods

Quartz doubly distilled water and polyethylene containers were used for the preparation of all aqueous solutions. All chemicals were at least of analytical grade unless otherwise stated. The colorimetric studies were all performed at 25°C.

2.1. Materials

$AlCl_3$ (Shanghai Chemicals Co., China) solution (0.25 mol/L): Al(III) concentration was calibrated by ICP-AES (JA1100, Kempston Controls, USA). NaOH solution (0.25 mol/L) standardized by potassium hydrogen phthalate (Chemical Reagent Co., Tianjin, China). The stock standard solution of $NaAl(OH)_4$ (0.100 M) was prepared by dissolving 0.677 g of Al power (99.99%, Shanghai, China) in 35.0 mL NaOH (4.0 M) and then diluting it to 250 mL with water. Ferron colorimetric solution was prepared as reported in the literature [24].

Preparation of HPAs with different OH/Al molar ratios [22,25,26]: appropriate volume of 0.25 mol/L NaOH solution was added dropwise (1.8 ± 0.2 mL min^{-1}) to a 14.0 mL of 0.25 mol/L $AlCl_3$ solution maintained at 80°C under fast stirring (1020±10 rpm). The volumes of NaOH added varied with the target OH/Al (0.5, 1.0, 1.4, 1.7, 2.0, and 2.3). After the titration of NaOH was completed, the resulting solutions were continuously heated and stirred at 80°C for another 30 min. Then, the final volume of every sample was adjusted to 50 mL with water. After aging for 24 h at room temperature, the sample solutions were further analyzed. The total Al concentrations in these HPAs were all 7.1×10^{-2} mol/L.

Purified K-Al_{13} solution was prepared and purified from the HPAs with OH/Al = 2.3 by SO_4^{2-}/Ba^{2+} method. Its total Al was 2.9×10^{-2} mol/L, which was determined by ICP-AES. K-Al_{13} sulfate tetrahedral-shape crystals and obtained K-Al_{13} solution were examined with XRD (Philips X' Pert Pr X-ray Diffractometer, Cu Kα radiation of wavelength 1.5418 Å) and ^{27}Al NMR (DRX-500, Bruker,Germany), respectively (Fig. 1).

As shown in Fig. 1a, only two peaks were detected: one resonance peak of $Al(OH)_4^-$ at 80 ppm is the reference peak, and the other is at 62.5 ppm, which belongs to the resonance peak of AlO_4 located in the center of the Al_{13} polycation. This result indicated that the K-Al_{13} solution was high purity. In Fig. 1b, d value of the three strongest characteristic peaks were 1.023, 0.513 and 0.343 nm, which is in perfect accordance with the results determined in literature [27].

2.2. *Effect of different [Ferron] on the determination of [Al_b] in HPAs*

Four concentration levels (K-Al_{13} solutions, [Al_T] = 2.1×10^{-5}, 4.0×10^{-5}, 6.3×10^{-5}, 8.0×10^{-5} mol/L; HPAs with OH/

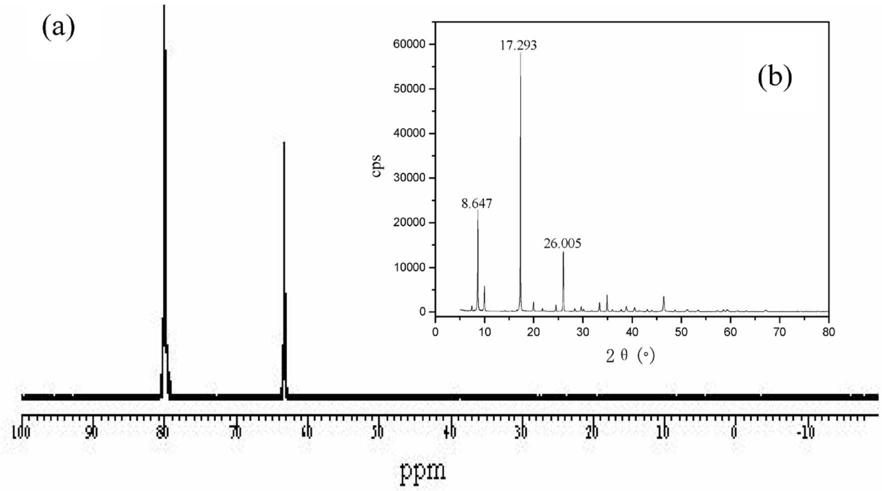

Fig. 1. (a) ^{27}Al NMR spectra of the K-Al_{13} solution; (b) XRD spectra of K-Al_{13} sulfate tetrahedral-shape crystals.

Al = 0.5~2.3, $[Al_T]$ = 2.0×10^{-5}, 4.0×10^{-5}, 6.0×10^{-5}, 8.0×10^{-5} mol/L) were employed to perform this study. A certain amount of sample was transferred into appropriate volume of water, followed by addition of Ferron colorimetric solution. For each $[Al_T]$ level, various [Ferron] were used: 2.0×10^{-4}, 4.0×10^{-4}, 8.0×10^{-4}, 1.2×10^{-3}, 1.6×10^{-3}, 2.0×10^{-3}, 2.4×10^{-3}, 3.0×10^{-3} and 4.8×10^{-3} mol/L. The final volume was 25 mL, mixed well (pH = 5.2 ± 0.2). Then, kinetic scan for these solutions (pH = 5.2 ± 0.2) was initiated at 370 nm against the respective reagent blank. The scan frequency was 15 points/min, and the duration was 120 min (UV-Vis3600, SHIMADZU, Japan; 1 cm quartz cell).

Calculation of $[Al_b]$, the absorbance corresponding to the mononuclear Al subtracts from that determined at 120 min on the A-t curves. The difference-value was converted to the concentration according to the standard curve. This concentration is $[Al_b]$ [28].

2.3. ^{27}Al nuclear magnetic resonance spectroscopy

The instrumental main settings and data acquisition conditions were set length = 0.4 s, spectra (n) = 200, delay for pulse length–delay–set length sequence = 500 µs, temperature = 300 K, pulse length = 12 µs, spectrum width = 40 KHz, delay = 0.5 s. For the coaxial NMR tubes, a 5 mm NMR tube was used with a 1 mm tube, held in a coaxial position by a pressure-equalizer plug. The sample (0.8 mL) was held in the 5 mm NMR tube. To the 1 mm tube in this case were added equal volumes of standard $NaAl(OH)_4$ solution and D_2O (100 µL), which served as both quantitative reference and lock, respectively [20,23,29,30]. The standard curve of ^{27}Al NMR determination was prepared by plotting the integrated intensity (S) of the ^{27}Al NMR determination for $[Al(H_2O)_6]^{3+}$ against Al:

$$[Al](mol/L) = (5.99 \times 10^{-5}) \times S,\ R^2 > 0.999 \quad (1)$$

3. Results and discussion

3.1. Effect of [Ferron] on the accurate determination of $[Al_b]$ in HPAs

3.1.1. K-Al_{13} solutions

For K-Al_{13} solutions, as shown in Fig. 2a, the reaction between Al_b and Ferron was accelerated with increase of [Ferron], and the slope of the rising part on the A-t curves was gradually increasing. The time it took for this reaction to reach equilibrium was decreased. Thus, [Ferron] can directly affect the reaction extent between K-Al_{13} and Ferron, and then affect the accurate determination of $[Al_b]$.

Also, it can be seen from Fig. 2b that the change of $[Al_b]$ with [Ferron] increase all presented a regular trend: the increase of [Ferron] resulted in the rising of $[Al_b]$ at [Ferron] <1.6×10^{-3} mol/L (dashed line L in Fig. 2b), and then $[Al_b]$ maintained small fluctuations nearby a constant value (95%) when [Ferron] was 1.6×10^{-3}~3.0×10^{-3} mol/L. So, within this range, the dosage of Ferron in chromogenic reaction system is sufficient, Al_b can be completely dissociated and complexed. Then, a gradual decrease presented from [Ferron]>3.0×10^{-3} mol/L (dashed line H in Fig. 2b), which is due in part to the big background disturbance introduced by higher dosage of chromogenic agent, as well as the formation of dimer of Ferron. The reaction activity between Al_b and this dimer reduces, which directly results in the low measuring result of $[Al_b]$ [31]. Thus, in K-Al_{13} solutions with the same $[Al_T]$, variation of [Ferron] obviously influences the determination of $[Al_b]$. Only when [Ferron] was 1.6×10^{-3}~3.0×10^{-3} mol/L, Al_b in the K-Al_{13} solutions with $[Al_T]$ = 2.0×10^{-5}~8.0×10^{-5} mol/L could be complexed completely, the accurate determination of $[Al_b]$ could be achieved. In this study, in order to avoid the boundary conditions, [Ferron] = 2.0×10^{-3}~3.0×10^{-3} mol/L was recommended for the accurate determination of $[Al_b]$ in K-Al_{13} solutions. Some K-Al_{13} solutions, which were also obtained from SO_4^{2-}/Ba^{2+} method, reported in the literature had $[Al_b]$: 99%, 95% and 96% [16,32,33]. These results are comparable to $[Al_b]$ obtained in this study.

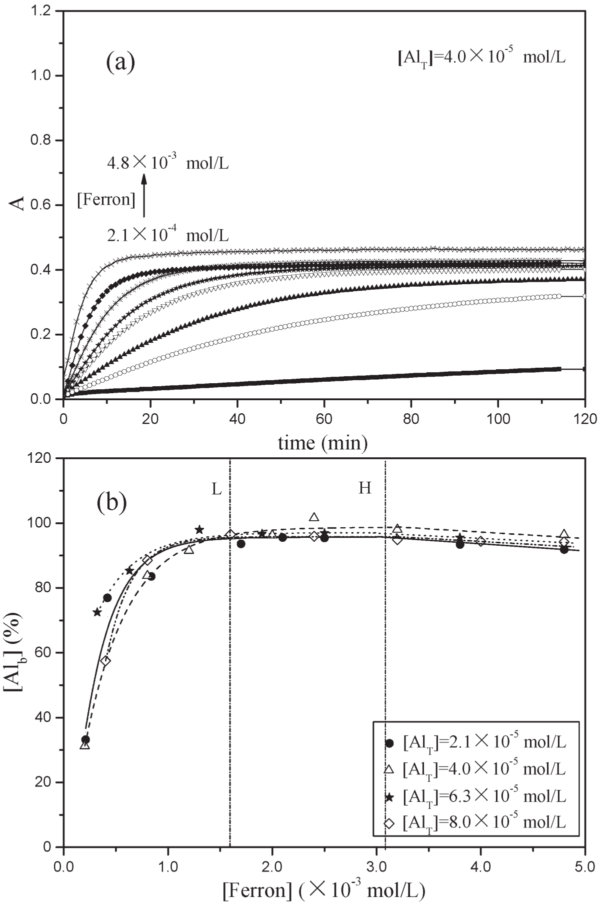

Fig. 2. (a) A-t curve determined in the four Al(III) concentrations of K-Al_{13}-Ferron colorimetric solutions at different [Ferron] ($[Al_T]$ = 4.0×10^{-5} mol/L: [Ferron] = 2.0×10^{-4} mol/L (■), 8.0×10^{-4} mol/L (○), 1.2×10^{-3} mol/L (▲), 1.6×10^{-3} mol/L (▽), 2.0×10^{-3} mol/L (★), 2.4×10^{-3} mol/L (☆), 3.2×10^{-3} mol/L (◆), 4.8×10^{-3} mol/L (×)); (b) The changing law of $[Al_b]$ with varied [Ferron] in the K-Al_{13} solutions with four levels of Al concentration (λ_{max} = 370 nm, pH = 5.2±0.2, T = 25°C).

3.1.2. HPAs with different OH/Al molar ratios

The species of Al_b in K-Al_{13} solutions is relatively simple. In order to deeply study color developing characterization of HPAs containing various species under different [Ferron] conditions, 6 HPAs (OH/Al = 0.5, 1.0, 1.4, 1.7, 2.0, 2.3) were selected. The results shown in Fig. 3 indicated that [Ferron] was also a key factor influencing the changing trend of A-t curves determined in the HPA-Ferron systems, which was similar to that shown in the K-Al_{13}-Ferron system. With the increases of [Ferron] in the color developing system, the reaction rate between Al_b and Ferron was accelerated, the slope of the rising part on these A-t curves was gradually increasing. Thus, the time it took for this reaction to reach equilibrium was decreased.

Two changing trends of $[Al_b]$ with [Ferron] increase can be confirmed in the HPAs with different OH/Al molar ratios (Fig. 4): for the HPAs with OH/Al = 0.5~1.4, $[Al_b]$ gradually increased with the increase of [Ferron]. When [Ferron] reached 1.6×10^{-3} mol/L, $[Al_b]$ was at its maximum (17%, 32% and 45%). This trend remained constant until [Ferron] = 4.8×10^{-3} mol/L. For the HPAs with OH/Al = 1.7~2.3, $[Al_b]$ also increased with the increase of [Ferron] when [Ferron] was less than 1.6×10^{-3} mol/L. At 1.6×10^{-3} mol/L≤[Ferron]≤3.0×10^{-3} mol/L, $[Al_b]$ reached the maximum (56%, 65% and 78%). Further increase of [Ferron] will result in the decrease of $[Al_b]$. According to the above results, for the HPAs with different OH/Al, the determination conditions of $[Al_T]$ = 2.0×10^{-5}~8.0×10^{-5} mol/L and [Ferron] = 2.0×10^{-3}~3.0×10^{-3} mol/L are proposed to achieve accurate determination of $[Al_b]$.

3.2. Comparison of $[Al_b]$ in the same HPAs determined at sufficient and insufficient [Ferron] conditions

According to the above experiment results, it can be explicit, in the HPA-Ferron chromogenic reaction system, the conditions of [Ferron]<1.6×10^{-3} mol/L and [Ferron]≥1.6×10^{-3} mol/L are the insufficient and sufficient dosage for Ferron respectively. The results summarized from literature (Table 1) indicated, for the HPAs (OH/Al = 0.5, 1.0, 1.4, 1.7, 2.0, 2.3), when the dosage of Ferron was sufficient and the detecting time was 120 min, $[Al_b]$ was 17%, 32%, 45%, 56%, 65% and 78%, respectively. At the same time, with the increasing of OH/Al (0.5→2.3), the influence of the decrease of [Ferron] on $[Al_b]$ determination gradually increased. When [Ferron] reduced from sufficient to insufficient (2.0×10^{-4} mol/L), the

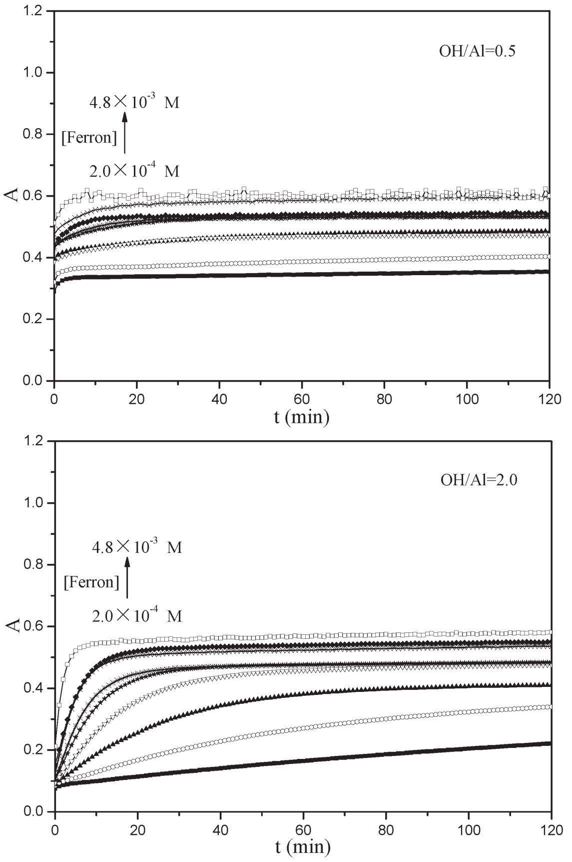

Fig. 3. A-t curve determined at $[Al_T]$ = 6.0×10^{-5} mol/L and increasing [Ferron] in theHPAs with different OH/Al molar ratios ([Ferron] = 2.0×10^{-4} mol/L (■), 4.0×10^{-4} mol/L (○), 8.0×10^{-4} mol/L (▲), 1.2×10^{-3} mol/L (▽), 1.6×10^{-3} mol/L (★), 2.0×10^{-3} mol/L (☆), 2.4×10^{-3} mol/L (◆), 3.0×10^{-3} mol/L (×), 4.8×10^{-3} mol/L (□); λ_{max} = 370 nm, pH = 5.2±0.2, T = 25°C).

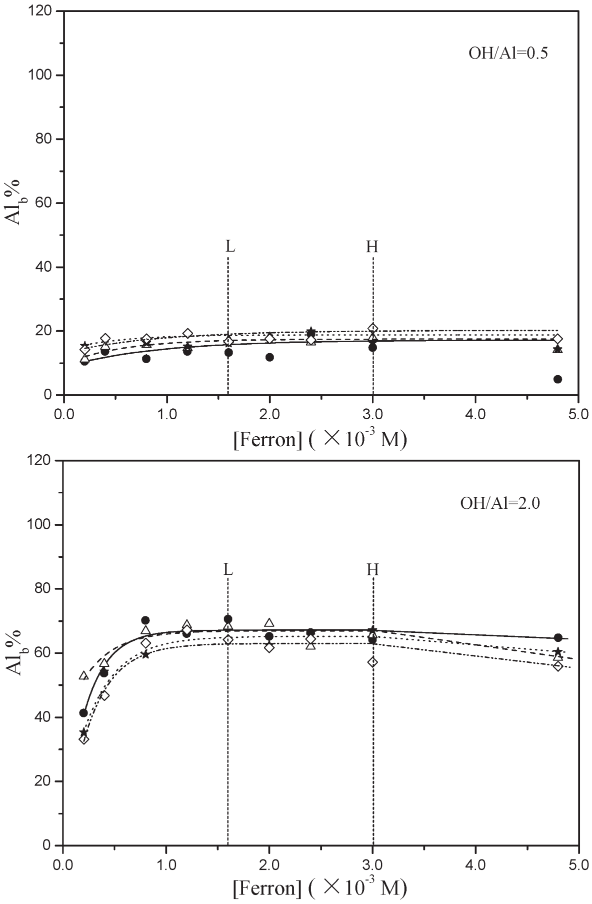

Fig. 4. The changing law of $[Al_b]$ with varied [Ferron] in the HPAs (OH/Al = 0.5, 2.0) with four levels of Al concentration($[Al_T]$ = 2.0×10^{-5} mol/L (●), 4.0×10^{-5} mol/L (△), 6.0×10^{-5} mol/L (★), 8.0×10^{-5} mol/L (◇); λ_{max} = 370 nm, pH = 5.2±0.2, T = 25°C).

Table 1
Comparison of [Al_b] in the same HPAs determined at sufficient and insufficient [Ferron]

[Al_T] [Ferron]		2.0×10^{-5} mol/L		4.0×10^{-5}mol/L		6.0×10^{-5}mol/L		8.0×10^{-5}mol/L	
		Al_b%	ΔAl_b (I-S)	Al_b%	ΔAl_b (I-S)	Al_b%	ΔAl_b (I-S)	Al_b%	ΔAl_b (I-S)
OH/Al = 0.5									
Insufficient	2.0×10^{-4} mol/L	10	–5	11	–6	15	–2	14	–4
	4.0×10^{-4} mol/L	14	–1	15	–2	18	+1	18	0
	8.0×10^{-4} mol/L	11	–4	16	–1	16	–1	18	0
	1.2×10^{-3} mol/L	14	–1	15	–2	15	–2	19	1
Sufficient (1.6×10^{-3}~3.0×10^{-3} mol/L)		15±3		17±1		17±2		18±2	
Literature value [34]									
Sufficient		Al_b% = 20%							
OH/Al = 1.0									
Insufficient	2.0×10^{-4} mol/L	18	–13	19	–12	20	–13	19	–15
	4.0×10^{-4} mol/L	25	–6	26	–5	25	–8	26	–8
	8.0×10^{-4} mol/L	28	–3	32	+1	30	–3	30	–4
	1.2×10^{-3} mol/L	34	+3	28	–3	28	–5	33	–1
Sufficient (1.6×10^{-3}~3.0×10^{-3} mol/L)		31±1		31±2		33±2		34±3	
Literature value									
5.6×10^{-4} mol/L[36]		Al_b% = 21%			ΔAl_b(I-S) = –11%				
Sufficient [34,35]		Al_b% = 33% , 31%							
OH/Al = 1.4									
Insufficient	2.0×10^{-4} mol/L	24	–20	29	–15	23	–23	22	–25
	4.0×10^{-4} mol/L	36	–8	38	–6	33	–13	36	–11
	8.0×10^{-4} mol/L	46	+2	47	+3	43	–3	45	–2
	1.2×10^{-3} mol/L	42	–2	47	+3	45	–1	45	–2
Sufficient (1.6×10^{-3}~3.0×10^{-3} mol/L)		44±5		44±2		46±1		47±1	
OH/Al = 1.7									
Insufficient	2.0×10^{-4} mol/L	36	–19	35	–18	32	–25	31	–26
	4.0×10^{-4} mol/L	38	–17	44	–9	48	–9	42	–15
	8.0×10^{-4} mol/L	54	–1	52	–1	55	–2	54	–3
	1.2×10^{-3} mol/L	49	–6	56	+3	56	–1	56	–1
Sufficient (1.6×10^{-3}~3.0×10^{-3} mol/L)		55±2		53±2		57±2		57±2	
OH/Al = 2.0									
Insufficient	2.0×10^{-4} mol/L	41	–26	53	–13	35	–30	33	–29
	4.0×10^{-4} mol/L	54	–13	57	–9	54	–11	47	–15
	8.0×10^{-4} mol/L	70	+3	67	+1	60	–5	64	+2
	1.2×10^{-3} mol/L	66	–1	69	+3	66	+1	67	+5
Sufficient (1.6×10^{-3}~3.0×10^{-3} mol/L)		67±3		66±3		65±2		62±3	
Literature value									
5.6×10^{-4}mol/L[36]		Al_b% = 35%			ΔAl_b(I–S) = –30%				
Sufficient [35]		Al_a% = 73%							
OH/Al = 2.3									
Insufficient	2.0×10^{-4} mol/L	34	–48	32	–50	51	–26	50	–22
	4.0×10^{-4} mol/L	58	–24	61	–21	70	–7	55	–17
	8.0×10^{-4} mol/L	76	–6	83	+1	76	–1	73	+1
	1.2×10^{-3} mol/L	79	–3	83	+1	74	–3	73	+1
Sufficient (1.6×10^{-3}~3.0×10^{-3} mol/L)		82±8		82±5		77±3		72±6	

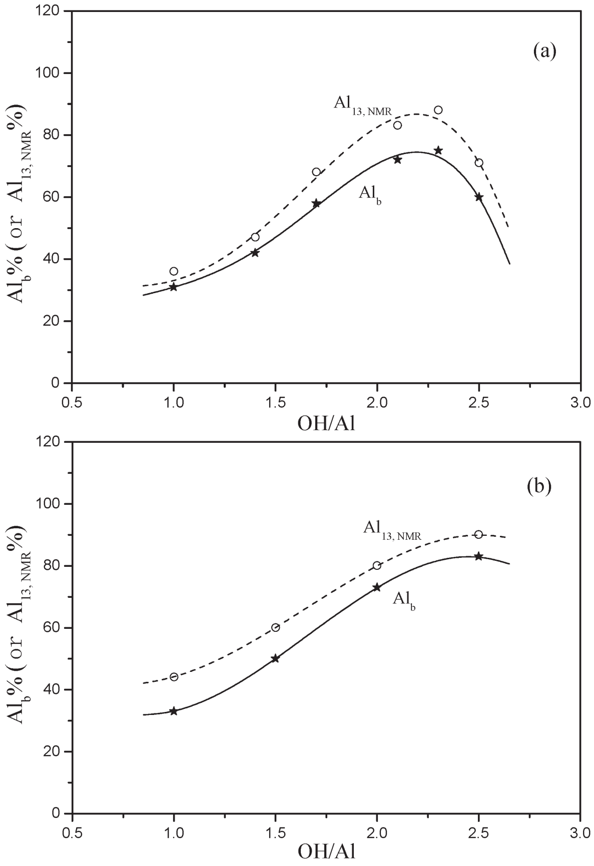

Fig. 5. Comparison between [Al_b] and [K-Al_{13}] in the HPAs with different OH/Al molar ratios (This study (a)Detecting condition: [Ferron] = 2.1×10^{-3} mol/L, [Al_T] = 4.2×10^{-5} mol/L; ^{27}Al NMR: [Al] = 7.1×10^{-2} mol/L; Literature (b) Detecting condition in Literature: [Ferron]≥1.6×10^{-3} mol/L, [Al_T] = 5.3×10^{-5} mol/L; ^{27}Al NMR: [Al] = 0.10 mol/L).

reduction of [Al_b] was 1%~6%, 1%~15%, 1%~25%, 1%~26%, 1%~30% and 1%~50%, respectively.

The results reported in literature were that the dosage of Ferron was sufficient, [Al_b] in the HPAs with OH/Al = 0.5, 1.0 and 2.0 were 20% [34]; 31%, 33% [34,35]; 73% [35]. They are comparable to that obtained in this study. While, the reaction proposed in literature [36] was typical insufficient (Ferron] = 5.6×10^{-4} mol/L), [Al_b] in the HPAs with OH/Al = 1.0 and 2.0 was 21% and 35%. These results are in accordance with ours. The differences between Al_b determined at sufficient (32% and 65%) and insufficient conditions were 11% and 30%. This result is also in line with the conclusion drawn in this study.

3.3. Comparison between [Al_b] and [K-Al_{13}] in the HPAs with different OH/Al molar ratios

As shown in Fig. 5a, at the optimal chromogenic reaction conditions, in the same HPAs, [Al_b] was less than [$Al_{13,NMR}$], that is:

$$\Delta Al_b = [Al_{13,NMR}]-[Al_b]>0 \tag{2}$$

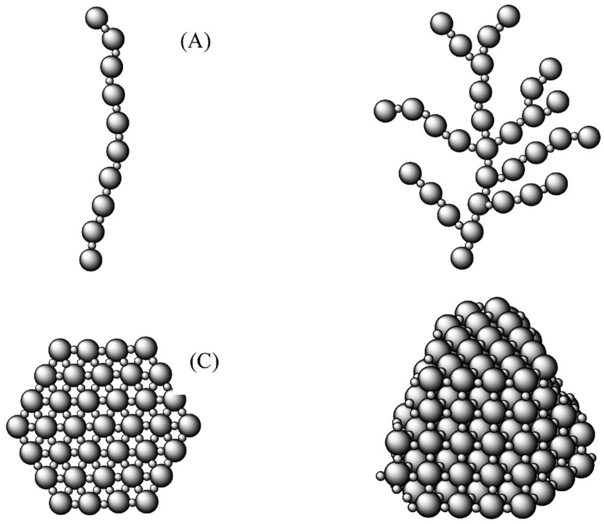

Fig. 6. The model of K-Al_{13} aggregation (the big ball is Al_{13}^{7+} and its diameter is 12 Å; the small ball is Cl^- and its diameter is 3.6 Å. A: Linear; B: Branched; C: Surface; D. Random aggregation of sol particles).

Moreover, the average value of ΔAl_b% in these solutions was +8.9%. Analyzing the literature results (Fig. 5b), the chromogenic reaction is the best conditions defined by this study [35], [$Al_{13,NMR}$]–[Al_b]>0 and the average value of ΔAl_b% was +8.6%, which is in accordance with this study. In consequence, when the conditions of HPA-Ferron chromogenic reaction is in the optimal range, the difference law between [Al_b] and [$Al_{13,NMR}$] proposed in this study is correct.

For ΔAl_b>0, it can be illustrated by the aggregation of K-Al_{13} (Fig. 6). There is no direction and saturation for ionic bond, which provides maximum likelihood for the aggregation of K-Al_{13}. The driving force of this aggregation mainly comes from the concomitant contra-ion, Cl^-, in HPAs. Hydrogen bond formed between H_2O on K-Al_{13} ionic also has certain contribution. Then the possible aggregation morphology includes linear, branched, surface type and even random aggregation of sol particles [37–41]. For those K-Al_{13} aggregations with linear and lesser degree of branching, it is easier for Ferron reagent to dissociate them and Al_{13} can be released one by one, then chromogenic assay can be achieved. But for the K-Al_{13} aggregations with surface type and three-dimensional structure, due to the increase in binding extent and steric hindrance, dissociation and color reaction become rather difficult. While, AlO_4 nucleuses in these aggregations still keep the structure of symmetrical electronic environment, hence, it can be measured by ^{27}Al NMR [23,37].

4. Conclusions

Various [Ferron] used in HPA-Ferron reaction system obviously influences the chromogenic reaction between Al_b and Ferron, and further influences the accurate determination of [Al_b]. The following rules can be proposed according to the above research:

(1) For HPAs, $[Al_T]$ is in the range of 2.0×10^{-5}~8.0×10^{-5} mol/L, [Ferron] should be 2.0×10^{-3}~3.0×10^{-3} mol/L, where for those HPAs with different $[Al_T]$, $[Al_b]$ can be achieved accurate determination.

(2) Insufficient dosage of Ferron results in a low measurement of $[Al_b]$, which increases with gradual increase of OH/Al molar ratio.

(3) Under the optimal conditions of Ferron chromogenic, the difference law between $[Al_b]$ and $[Al_{13,NMR}]$ in the HPAs with different OH/Al molar ratios is: $\Delta Al_b = [Al_{13,NMR}]–[Al_b]>0$。

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