



Hydrolyzed Al(III) clusters: Speciation stability of nano- Al_{13}

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Abstract

Pure nano- Al_{13} and aggregates at various concentrations were prepared to examine the particle size effect of coagulation with inorganic polymer flocculant. The property and stability of various species formed were characterized using Infrared, ^{27}Al -NMR, photo correlation spectroscopy (PCS), and Ferron assay. Results showed that concentration and temperature exhibited different roles on the stability of Al_{13} . The quantity of Al_b species analyzed by ferron assay in the initial aging period corresponded well with that of Al_{13} , which has been confirmed in a dimension range of 1–2 nm by PCS. Al_{13} solutions at high concentrations (0.5–2.11 mol/L) were observed to undergo further aggregation with aging. The aggregates with a wide particle size distribution would contribute to the disappeared/decreased Al_{13} basis on the ^{27}Al -NMR spectrum, whereas a part of Al_{13} would still remain as Al_b . At low concentrations, Al_{13} solution was quite stable at normal temperature, but lost its stability quickly when heating to 90°C.

Key words: nano- Al_{13} ; clusters; inorganic polymer flocculant; speciation stability

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Introduction

Inorganic polymer flocculants (IPFs) are widely applied as special chemical reagents in water and wastewater treatment processes. Compared with the traditional coagulants, IPFs can give markedly improved coagulation effects, and show many advantages such as low dosage, efficient sedimentation, low sludge volume and flexibility to various water quality conditions (Gray et al., 1995; Tang, 1998; Solomentseva et al., 1999; Wang and Tang, 2001; Wang et al., 2002). Therefore, IPFs have the potential to become the main reagents for water and wastewater treatment. Among the IPFs, polyaluminum chloride (PACl) is the most efficient, widely applied coagulant.

PACl is an intermediate product during the hydrolysis-polymerization-precipitation process of Al(III) ions under specific conditions. A large amount of investigation and practical application show that $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}^{7+}$ (simplified as Al_{13}) is the most efficient species in PACl coagulant (Gray et al., 1995; Tang, 1998; Solomentseva et al., 1999; Wang and Tang, 2001; Parthasarathy and Buffle, 1985; Benschoten and Edzwald, 1990; Furrer, 1993; Matsui et al., 1998; Xu et al., 2003; Wang et al., 2004). The content of Al_{13} is therefore the main quality index in PACl products besides the basicity, i.e., OH/Al mole ratio. In current

industrial PACl products, Al_{13} content shown as Al_b with ferron assay is normally less than 40% (Wang et al., 2004). In some cases, it remains a minor component in the products (Tang, 1998).

To prepare PACl with high content Al_{13} -nanoflocculant (containing more than 70% Al_{13}) or pure Al_{13} have become recently the target in the research of IPFs. This is also of interest in several other fields such as catalysis, pharmaceuticals, paper industry (Teagarden et al., 1981; Pinnavia, 1983). However, due to the quite complicated nature of Al(III) hydrolysis, the properties of Al_{13} -nanoflocculant need further exploration.

The objective of this study is to investigate the stability of Al_{13} at various concentrations using IR, ^{27}Al -NMR, photo correlation spectroscopy (PCS), and Ferron assay in combination. The pathway of species transformation is also proposed.

1 Materials and methods

1.1 Preparation of Al_{13}

The separation and preparation of pure Al_{13} was carried out as shown in a previous publication (Xu et al., 2003). Batches of purified Al_{13} samples were mixed together and freeze-dried to white solid powder. Different purified Al_{13} solutions were then prepared by dissolving a certain

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amount of the powder into distilled water to desired concentrations, i.e., 0.01–2.1 mol/L. The total aluminum concentration, and speciation distribution were further characterized by IR, Ferron assay, ^{27}Al -NMR, and PCS.

Samples with different concentrations were aged at room temperature and analyzed at certain period during aging process. To examine the effect of temperature, 20 mL of the newly prepared 0.11 mol/L solution was transferred into three 50 mL conical flasks and aged at room temperature (22–25°C), and 55 and 90°C with a constant temperature water-bath. After certain times, samples were taken out for analysis.

1.2 Al-ferron assay

The basic procedure of Ferron assay has been described elsewhere (Wang et al., 2004). The pre-mixed ferron solution of 5.5 mL was pipetted into a 25-mL graduated glass tube and then diluted with distilled water. After homogeneous mixing, the reacting sample was added quickly to a 1-cm glass cuvette. The timed absorbance measurements (at 366 nm), using a DU650 Beckman UV-Visible spectrophotometer (USA), were carried out after 1 min and recorded for further 2 hr. Operationally, 1 min absorbance was defined as Al_a , while the consequently developed from 1 min to 2 hr was defined as Al_b . Then Al_c was calculated as the difference between total Al (Al_t) and $\text{Al}_a + \text{Al}_b$.

1.3 ^{27}Al -NMR analysis

The solution was examined using 500 MHz ^{27}Al NMR spectroscopy (Advance Drx 500 Bruker, Germany). The experimental conditions are: NS = 128, P1 = 14.00 s, PL₁ = -3.00 dB, O₁P: 47.38; DW: 19.20, solvent: D₂O, and temperature 298 K. The external standard used is 0.05 mol/L NaAlO₂ (with 75% D₂O).

1.4 PCS characterization

The basic procedure of PCS analysis was addressed by Xu et al. (2003). Samples were filtered twice using 0.45 μm Millipore membrane and then put into the clean sample bottle. The samples were measured at an angle of 90° by using BIC 9000SM laser light scattering instrument (BIC Company, USA).

1.5 IR characterization

The IR characterization was carried out by using NEXUS 670X. Samples (1–2 mg) were mixed with 100 mg KBr as carrier. Under the pressure of 10 atm, the samples were made into transparent slices. It should be noted that the samples and KBr must be dried before preparation.

2 Results and discussion

2.1 Characterization of Al₁₃

Speciation of prepared Al₁₃ solutions was analyzed by Ferron assay and ^{27}Al NMR as shown in Table 1 and Fig. 1. It can be seen that the samples prepared at

concentrations of 0.10–2.1 mol Al/L contain mainly Al_b species. Al_c fraction does not exist significantly as the ferron method has the typical analytical errors of around 1%. It seems also that Al_a fraction could be contributed from surface Al of Al₁₃, i.e., as the results of the rapid dissolution/dissociation of surface Al by ferron. It needs to be noted that the speciation characterization by ferron method is operationally defined, i.e., Al_a is the fraction reacted suddenly in 1 min. Some researchers define the Al_a fraction reacted in 30 sec (Parker and Bertsch, 1992). Therefore, the Al_a calculated here is significantly high. Samples obtained contain therefore mainly Al₁₃ species. It indicates that the Al₁₃ samples prepared can be diluted into various concentrations. High concentration Al₁₃ solutions are relatively stable and become therefore the valid proof for a commercial preparation. From the ^{27}Al -NMR results in Fig. 1, it can be seen that only sharp single response at 63.0 ppm. No peak of Al_m (monomer) at 0 ppm or other species can be observed for all the samples. And the peak area at 63.0 ppm increases rapidly with increasing Al_t concentration. A very good linear equation with R² of 0.9996 can be yield, i.e., $y = 4.085x + 0.0231$, where y is the peak area, and x is the concentration. It indicates that the only one species observed in the above samples is Al₁₃. The results show that the Al₁₃ detected by ^{27}Al -NMR has good relation with Al_b under these conditions.

In addition, the solid powder of purified Al₁₃ sample and sulfate salts have been analyzed by IR, which is shown in Fig. 2. It can be seen that the frequency between 3500–3400 cm⁻¹ is the vibration of -OH group, reflecting the complexation of OH-Al. And the frequency at 2400 cm⁻¹ is the vibration of Al-O, and 1640 cm⁻¹ shown as the structure combined water. The frequencies between 1000–400 cm⁻¹ are the vibration of surface -OH group.

Table 1 Speciation distribution of purified Al₁₃ solutions by Ferron assay

Al _t (mol Al/L)	Al _a (%)	Al _b (%)	Al _c (%)
0.11	2.31	97.33	0.36
0.42	2.06	97.38	0.56
1.06	2.02	96.80	1.18
2.11	1.91	96.59	1.60

Al_t: total aluminum concentration; Al_a: the fraction reacted suddenly within 1 min; Al_b: the fraction reacted quickly between 1 min and 2 hr, Al_c: the un-reacted fraction.

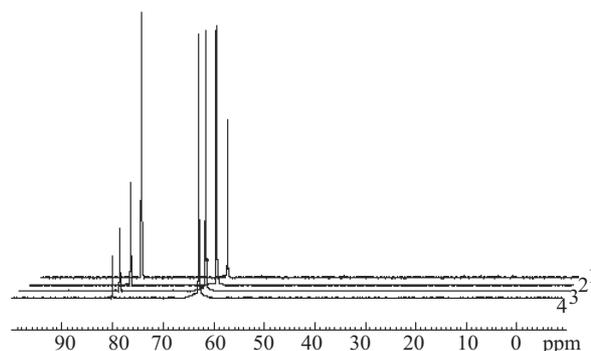


Fig. 1 Characterization of pure Al₁₃ by ^{27}Al -NMR after one week aging. Al_t for the samples 1, 2, 3, 4 is 0.11, 0.42, 1.06, and 2.11 mol/L, respectively.

The spectra largely similar feature for the Al_{13} powder and its sulfate salts except that the latter shows a typical S–O vibration at 1117 cm^{-1} .

2.2 Effect of concentration on the stability of Al_{13}

The effect of concentration on the stability of Al_{13} was also investigated at various Al_{13} solutions with ferron assay, as shown in Table 2. The speciation results from ferron assay show that Al_{13} is in a state of pseudo-stability and tends to aggregate with aging. Concentrations above 0.5 mol/L play a significant role on its stability. It explains partially the reason why Al_{13} sharply decreased during preparation of PACl at concentrations higher than 0.5 mol/L (Gray et al., 1995). Slow aggregation occurred for Al_{13} of 2.11 Al mol/L and the solution becomes turbid after one week. Moreover, there is only 86.79% of Al_b remaining after one month aging. However, the 0.11 mol/L Al_{13} shows quite stable feature and undergoes only minor change during one month aging. This has also been confirmed by NMR analysis as shown in Table 3. From the one week aging results in Fig. 1, it seems again that 0.11 mol/L solution exhibits quite good stability at ordinary temperatures. With increasing concentration, the speciation stability decreases gradually. The quantity of Al_{13} decreases 8% and 25% for solutions at 1.06 and 2.11 mol/L , respectively. While in ferron assay, the Al_b fractions are 95% and 87% after one week, i.e., decrease only 2% and 10%, respectively. This indicates that the decreased Al_{13} in ^{27}Al -NMR spectrum corresponds only partially with the remaining Al_b fraction after aging.

The particle size distribution of Al_{13} solutions after aging was also characterized by PCS. The results are shown in Table 4 and Fig. 3. It is observed that the particle

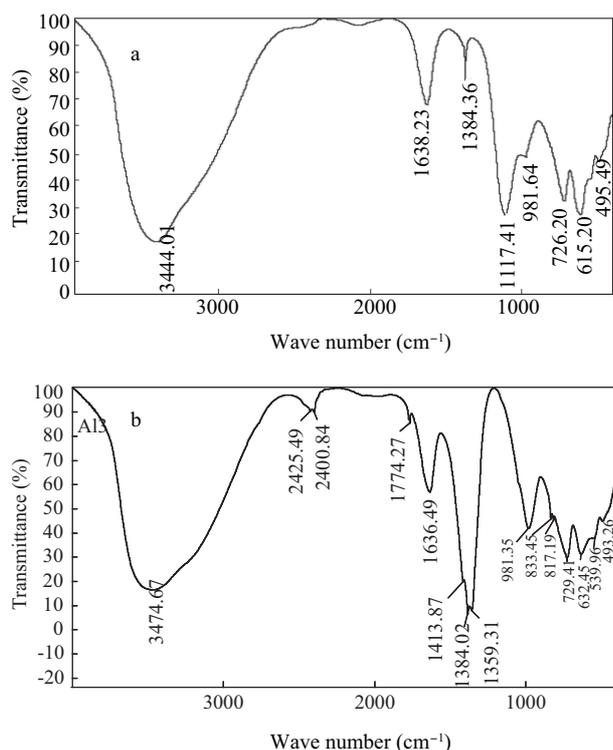


Fig. 2 IR spectra of solid Al_{13} sample. (a) Al_{13} sulfate; (b) Al_{13} .

Table 2 Stability of pure Al_{13} solutions measured by Ferron assay

Al_t (mol/L)	Aging (day)	pH	Observation	Al_a (%)	Al_b (%)	Al_c (%)
0.11	0	5.50	Clear	2.31	97.33	0.36
	1	5.51	Clear	1.58	97.51	0.90
	7	5.42	Clear	1.43	97.44	1.13
	30	5.27	Clear	1.21	94.81	3.98
0.42	0	5.16	Clear	2.06	97.38	0.56
	1	5.15	Clear	0.96	97.20	1.84
	7	5.00	Clear	1.80	94.71	3.49
	30	4.83	Some precip.	2.42	86.16	11.42
1.06	0	4.96	Clear	2.02	96.80	1.18
	1	4.93	Clear	1.08	96.07	2.85
	7	4.88	Some precip.	1.01	94.49	4.50
	30	4.67	Some precip.	0.93	85.70	13.37
2.11	0	4.81	Clear	1.91	96.59	1.50
	1	4.80	Clear	0.47	90.27	9.26
	7	4.70	Turbid	0.86	86.79	12.35
	30	4.36	Turbid	1.04	77.31	21.65

Al_t : total aluminum concentration; Al_a : the fraction reacted suddenly within 1 min; Al_b : the fraction reacted quickly between 1 min and 2 hr; Al_c : the un-reacted fraction.

Table 3 Speciation of pure Al_{13} solutions under aging by ^{27}Al -NMR analysis

Al_t (mol/L)	Time (day)	^{27}Al -NMR		
		$\delta = 80$ (refer.)	$\delta = 63$ (peak area %)	
0.11	0	1.000	0.55	101.58
	7	1.000	0.54	99.75
0.42	0	1.000	2.70	100.63
	7	1.000	2.66	99.15
1.06	0	1.000	4.23	97.03
	7	1.000	3.88	88.93
2.11	0	1.000	8.60	100.69
	7	1.000	6.50	75.12

size distribution (PSD) of Al_{13} solutions exhibit different features on aging, depending on the concentration. At low concentrations, Al_{13} exhibits only weak light scattering because of its small particle size. The scattering intensity is not strong enough to give precise analysis. An increasing intensity can be observed from 4.8 to 13.7 kcps for the 1.06 and 2.11 mol/L solutions. The PSD exhibits a mono-modal distribution around 2 nm , close to the reported dimension of Al_{13} . During aging, aggregation of Al_{13} occurs, as shown by stronger scattering intensity. Double peak distribution and triple peak distribution appear gradually with aging especially at higher concentrations. After 7 days aging, particle size of 0.11 mol/L Al_{13} increases to $4\text{--}5\text{ nm}$, while the 0.42 mol/L sample exhibits two-peak distribution feature with 84.79% the particles around 10 nm and 15.21% around $47.93\text{--}64.39\text{ nm}$. The sample of 1.06 mol/L exhibits also two-peak distribution with 85.59% at $34\text{--}40\text{ nm}$ and the other around $69.88\text{--}83.27\text{ nm}$. However, three-peak distribution exhibits with $27\text{--}34\text{ nm}$ (28%), $118\text{--}193\text{ nm}$ (5%) and $359\text{--}664\text{ nm}$ (67%) for the sample of 2.11 mol/L . It shows that most of the particles become as large as in the dimension of several hundred of nms.

It needs to be noted that there are limitations for the PCS analysis. The precise analysis of PSD remains a problem for PCS. The presence of large particles will affect the

Table 4 Change of particle size distribution (PSD) of Al₁₃ solution with aging by PCS analysis

Al _t (mol/L)	Aging (day)	Inten. (kcps)	PSD (nm)	Peak (%)	Al _t (mol/L)	Aging (day)	Inten. (kcps)	PSD (nm)	Peak (%)
0.11	1	–	–	–	0.42	1	–	–	–
	7	5.4	4.28–5.85	99.84		7	24.3	10.18–12.70	84.79
	15	9.8	11.53–14.73	79.68		15	28.3	47.93–64.39	15.21
			44.30–72.27	20.02				31.78–39.52	92.00
			124.8–170.1	84.21				79.38–98.71	8.00
1.06	1	4.8	26.54–36.17	15.79	2.11	1	13.7	38.96–55.40	24.16
			124.8–170.1	84.21				148.5–211.1	75.84
	7	29.5	34.66–39.88	85.59		7	503.9	26.97–34.50	28.10
			69.88–83.27	14.41					118.3–193.6
	15	34.3	34.75–45.40	61.38		15	537.6	28.00–50.31	28.32
			101.2–132.2	38.62					140.3–252.0
	30	56	34.02–42.61	51.04		30	604.8	29.82–47.70	4.15
			105.2–131.9	48.96					228.3–427.1
								934.5–2044	56.03

–: only very weak light scattering observed.

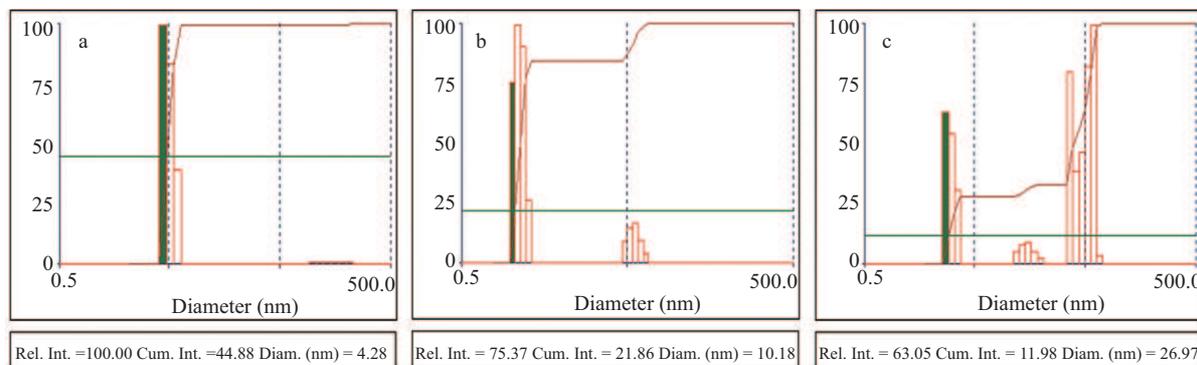


Fig. 3 PCS analysis of the Al₁₃ solutions at various concentrations. (a) Al_t = 0.11 mol Al/L for 2 days; (b) Al_t = 0.42 mol Al/L for 7 days; (c) Al_t = 2.11 mol Al/L for 7 days.

detection of small particles. However, the trend of particle size increasing with aging is clearly observed as shown by the increase of scattering intensity. Compared with the Ferron assay and ²⁷Al-NMR results, it seems that during aging the aggregates with a wide PSD contribute partially to the disappeared/decreased Al₁₃ in ²⁷Al-NMR spectrum while remaining in Al_b fraction.

2.3 Effect of temperature on the stability of Al₁₃

The 0.11 mol/L Al₁₃ was further aged under different temperatures and results are indicated in Fig. 4. The decrease of Al_b follows a pseudo-first order kinetic reaction. The kinetic constants are 0.0001, 0.0006, and 0.0197 hr⁻¹ at room temperature (22–25)°C, 55°C and 90°C, respectively. Figure 5 shows the NMR characterization of the samples aged at 90°C. It shows that Al₁₃ decreases markedly with aging time. The phenomenon is similar to those observed by ferron method. It should be noted that the peak of monomer Al appears after 24 hr aging, which indicates the dissolution of Al₁₃ during aging with heat.

The PCS results clearly show the particle aggregation feature of the samples heated under different conditions. It is observed that the initial solution scatters little light and shows little change for several days heating at 55°C. Results show that particles distribution are in the size range of 29–52 nm only after 10 days aging. However, heating at

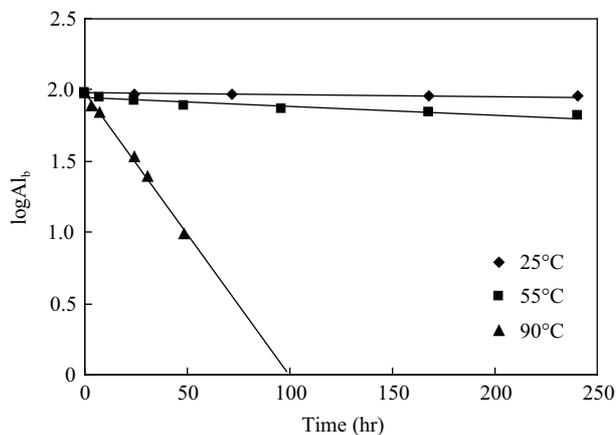


Fig. 4 Effect of temperature on the stability of Al₁₃.

90°C the scattering intensity increases quickly. Two-peak distribution is observed for 24 hr heating, with 60% of 200–260 nm and 40% of 600–700 nm. With further aging, the particle grows markedly and becomes 60% at 700 nm for 48 hr.

3 Discussion

The experimental results show that temperature has a significant effect on the transformation of Al₁₃. At room

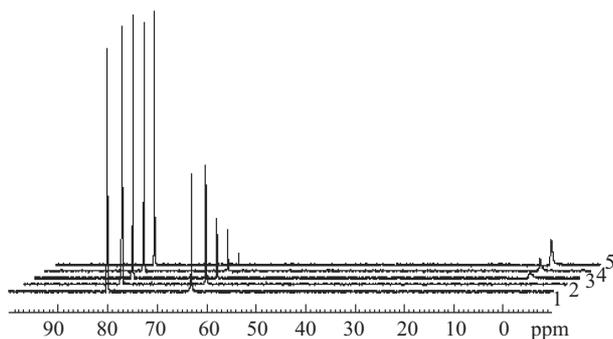
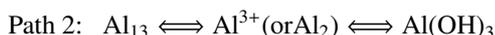
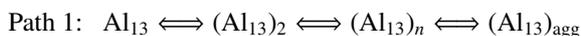


Fig. 5 ²⁷Al NMR analysis for Al₁₃ aged under 90°C at different periods. (1) 0; (2) 3 hr; (3), 24 hr; (4) 31 hr; (5): 48 hr.

temperature, Al₁₃ remains stable for a long time. With the increase of temperature, the stability of Al₁₃ decreases markedly and transformation to other species occurs quickly. There are two possible pathways of aggregation: one goes to soluble high polymers, the other one is to form solid Al(OH)₃ species as follows.



The exact pathway will depend on the presence of nuclei and their quantity. With the presence of nuclei, Al₁₃ will be depolymerized/dissolved into dimer or monomer, and then deposited onto the nuclei to form Al(OH)₃ precipitate. In the absence of nuclei, Al₁₃ will aggregate to form large particles, which would depend on the solution conditions. The follow-up step will be structure re-building and further transformation to Al(OH)₃ will be slower.

As shown in Table 2, the 2.11 mol/L Al₁₃ sample becomes turbid after 7 days aging. However, the Al_b from ferron assay remains as high as 86.79% and strong Al₁₃ signal is also observed as shown in ²⁷Al NMR. In contrast, the Al_b in the sample heated at 90° for 48 hr decreases rapidly to 9.7% and the solution becomes turbid also. There is a difference between the two processes. At high concentration, the aggregation between Al₁₃ units takes place and precipitates form finally after reaching certain size. The aggregates or precipitates formed can undergo rapid reaction with ferron and yield high Al_b also. However, when heated at high temperature, the Al₁₃ dissolves to form monomer or dimer as observed from ²⁷Al NMR and finally yield Al(OH)₃, which is formed irreversibly and does not react with ferron. Two pathways have been proposed for the aggregation of Al₁₃. Klopogge et al. (1992) considered that the decrease of Al₁₃ with little change of pH showed that the transformation of Al₁₃ was a kind of structure re-building, with no further hydrolysis involved. Many researchers agreed with this viewpoint and considered the final structure close to that of gibbsite (Tsai and Hsu, 1985; Bottero et al., 1987; Bradley et al., 1990), moreover, the crystal Al(OH)₃ was formed by free combination of Al₁₃ without re-hydrolysis. However, other researchers considered that the aggregation of Al₁₃ to form large particles resulted from the de-protonation in the edge or surface (Letterman and Asolekar, 1990). In the present study, it is also observed that the solution pH keeps

relatively stable during aggregation at high concentration, but not in the aggregation process at high temperature. This suggests that these two kinds of aggregation processes correspond well with the pathways shown above. The aggregation of Al₁₃ to form large particles increases mainly the degree of polymerization rather than changing the acid-base property. Therefore, the solution pH keeps relatively unchanged. The dissolution of Al₁₃ and further deposition onto nuclei will follow by the dissociation of H⁺. The solution pH then decreases. It should be noted that the two pathways will co-exist during aging of Al₁₃ under various conditions but one pathway will usually take the main role.

4 Conclusions

Pure Al₁₃ species exhibit certain stability. For the low concentration (Al_t < 0.11 mol/L), it can keep stable for a long time. With increasing concentration, the stability of Al₁₃ decreases and has the tendency to transform to other species but at relatively slow rate. On the one hand, Al₁₃ exhibits Keggin structure with AlO₄ in the center surrounded by 12 octahedral Al(III). Therefore protons cannot easily access the AlO kernel. On the other hand, this kind of structure results in the slow interchange of the inner-Al atom with the outer-Al atoms. The structure re-building and interchange of structural aluminum with bulk-aluminum is rather slow, so that the structure remains relatively stable.

The correspondence of Al₁₃ and Al_b is conditionally dependent. A good relationship exists for pure Al₁₃ solutions in the initial aging period. However, this relationship changes during further aggregation process. At room temperature, high solution concentration promotes aggregation of Al₁₃. The aggregates with a wide particle size distribution contribute partially to the disappeared/decreased Al₁₃ spectrum in ²⁷Al-NMR while remaining reactive with ferron as shown in Al_b fraction. The decreased Al₁₃ spectrum in ²⁷Al-NMR contributes partially to the remaining Al_b fraction during aging. At high temperature, the aggregates become relatively inert to react with ferron. However, part of the aggregates appears still as Al_b fraction while disappearing quickly from the ²⁷Al NMR spectrum.

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