

NOTES

²⁷Al NUCLEAR MAGNETIC RESONANCE AND FERRON KINETIC STUDIES OF PARTIALLY NEUTRALIZED AlCl₃ SOLUTIONS¹

Key Words—Aluminum, Ferron, Gibbsite, Hydroxy-Al complex, Nuclear magnetic resonance.

Although the existence of polynuclear OH-Al complexes in partially neutralized Al solutions has long been recognized, our understanding regarding their structures is still far from complete. Two models are commonly referred to in the literature:

Fragments of gibbsite. Brosset *et al.* (1954) and later Hsu (1977) proposed that the OH-Al polymers resemble fragments of crystalline aluminum hydroxide. In crystalline aluminum hydroxide, Al³⁺ ions are distributed in hexagonal rings, connected by OH-bridges. A necessary requirement for a stable structure is that the repulsion between Al³⁺ be balanced by the attraction of Al-OH-Al linkages. This principle should also hold for the OH-Al polymers in solution; i.e., if the OH-Al polymers are stable, the arrangement of Al³⁺ and OH⁻ ions in soluble polymers should follow a pattern similar to aluminum hydroxide solids. In the Al(OH)₃ structure, however, each OH⁻ at an edge is linked to only one Al³⁺ and is, therefore, in rapid equilibrium with the H⁺ in solution. The reported isoelectric point of aluminum hydroxide is in the pH range 8.0-9.2. Therefore, aluminum hydroxide particles, large or small, are always positively charged in acidic media, but the average net positive charge per Al atom increases with decreases in particle size. Extremely small particles having a high net positive charge per Al atom behave as true solutes and are defined as soluble polynuclear complexes.

Al-13 polymer. Johansson (1960, 1963) prepared well-crystallized basic aluminum sulfate or selenate by adding sodium sulfate or selenate to a partially neutralized Al salt solution of NaOH/Al molar ratio = 2.5. His X-ray powder diffraction structural analysis suggested that these crystals were composed of a basic unit of composition [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺. This structure consists of one Al³⁺ ion tetrahedrally coordinated to four O²⁻ ions, which, in turn, are surrounded by four

trioctahedral OH-Al configurations at the four corners of a truncated tetrahedron. He suggested that the OH-Al polynuclear complex in solution had the same configuration. The existence of this species in solution was also suggested by Aveston (1965) using ultracentrifugation and potentiometric titration, and by Rausch and Bale (1964) using small angle X-ray diffraction analysis. Akitt *et al.* (1972) and Akitt and Farthing (1978, 1981) observed two peaks having chemical shifts 63 ppm apart in their ²⁷Al nuclear magnetic resonance (NMR) spectra of partially neutralized Al solutions. One peak was attributed to monomeric Al ions; the other to the Al atom of the central AlO₄ group in the polymers. The NMR study was later corroborated by many others (Teagarden *et al.*, 1981; Bottero *et al.*, 1982; Bertsch, 1984; Bertsch *et al.*, 1986).

Neither of these two models, however, is adequate to describe the polynuclear OH-Al complexes in solution. Based on the kinetics of the Al-hydroxyquinoline reaction, Turner (1976a, 1976b) showed that the OH-Al polymers initially formed were not stable. During prolonged aging, this species gradually changed to another species of similar size and similar basicity, but was much more resistant to reaction with hydroxyquinoline. This conclusion was substantiated by Tsai and Hsu (1984, 1985) using the kinetics of Al-ferron color development and sulfate precipitation. In the present study, both the kinetics of Al-ferron color development and NMR spectroscopy are used to examine these two models.

EXPERIMENTAL

Partially neutralized AlCl₃ solutions were prepared and characterized with Al-ferron reaction kinetics and sulfate precipitation, following the procedures given in Tsai and Hsu (1984, 1985). The ²⁷Al NMR spectra of these solutions were recorded with a Varian Model FT-80 NMR spectrometer operating at 20.727 MHz. The spectrometer is equipped with a variable temperature, broad-band probe. The spectra were obtained using a 45° flip angle, a 1-s repetition rate, and no pulse delay.

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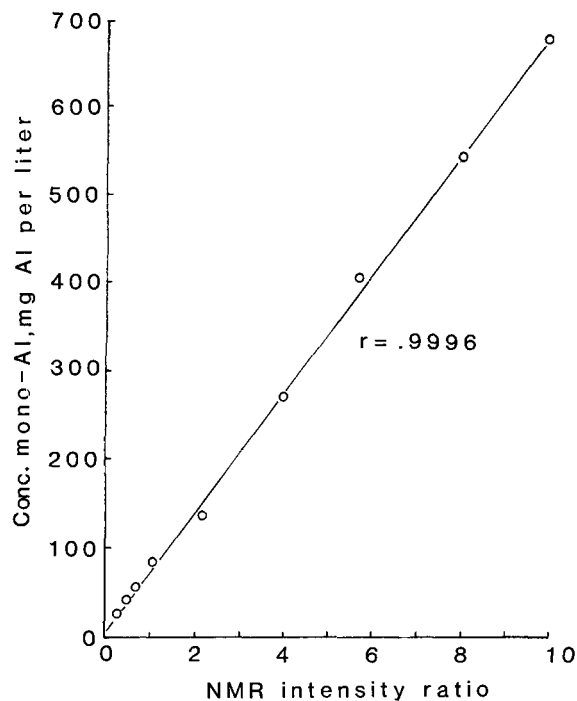


Figure 1. Correlation between the intensity of the ^{27}Al nuclear magnetic resonance (NMR) peak of chemical shift at 80 ppm and the concentration of monomeric Al ions (mg Al/liter). A freshly prepared 0.02 M $\text{Al}(\text{OH})_4^-$ solution was used as the reference with respect to the chemical shift and intensity in the NMR spectra.

A 16 K data table and a sweep width of 8 K were used to give a digital resolution of 1 Hz.

RESULTS AND DISCUSSION

In a preliminary experiment, the ^{27}Al NMR spectra of a series of AlCl_3 solutions were measured. The concentration ranged from 0.001 to 0.025 M. HCl was

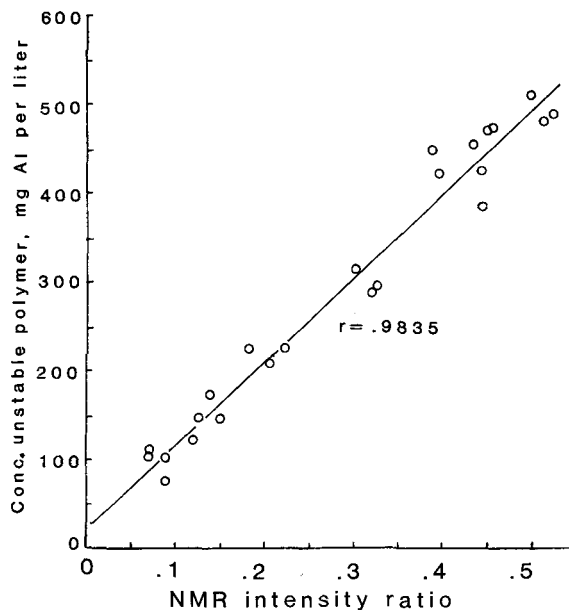


Figure 2. Correlation between the intensity of the ^{27}Al nuclear magnetic resonance (NMR) peak of chemical shift at 17 ppm and the concentration of unstable OH-Al polymer (mg Al/liter). The concentration of unstable polymers was estimated from Al-ferron kinetics. A freshly prepared 0.02 M $\text{Al}(\text{OH})_4^-$ solution was used as the reference with respect to the chemical shift and intensity in the NMR spectra.

added to each solution (H/Al molar ratio = 0.2) to suppress any possible hydrolysis and polymerization of Al^{3+} ions. A freshly prepared 0.02 M $\text{Al}(\text{OH})_4^-$ solution (NaOH/Al molar ratio = 5) in a capillary tube was inserted into the NMR sample tube. This solution served as a standard with respect to both chemical shift and the integrated area of the other peaks. One peak with a chemical shift of 80 ppm upfield from the $\text{Al}(\text{OH})_4^-$ reference was observed. The intensity ratio

Table 1. Distribution of Al ions (mg Al/liter) in OH-Al solutions of varying NaOH/Al ratio in preparation.¹

NaOH/Al molar ratio	NMR (ppm) ²		Al-mo ³		Al-usp ³		Al-sp ³ Ferron
	80	17	NMR ⁴	Ferron	NMR ⁵	Ferron	
0	7.67	nil	525	513	nil	(20)	nil
0.5	5.56	0.09	383	417	110	103	nil
1.0	4.35	0.205	302	317	218	208	7
1.5	2.72	0.325	192	204	331	296	10
1.8	2.14	0.393	153	123	395	423	15
2.0	1.448	0.448	107	84	447	471	15
2.2	0.965	0.52	74	47	514	489	16
2.5	nil	0.495	nil	tr	491	511	21

¹ Total Al = 540 mg/liter. Speciation of Al ions in solution was made using ^{27}Al nuclear magnetic resonance spectroscopy and the kinetics of Al-ferron reaction.

² Nuclear magnetic resonance (NMR) intensity ratio relative to reference.

³ Al-mo = monomeric Al; Al-usp = unstable OH-Al polymers; Al-sp = stable OH-Al polymers. Value in parenthesis was roughly estimated.

⁴ Calculated from the integrated area of peak at 80 ppm and Figure 1.

⁵ Calculated from integrated area of peak at 17 ppm and Figure 2.

Table 2. Distribution of Al ions in solution (mg Al/liter) as a function of duration of aging.¹

Aging time (days)	NMR (ppm) ²		Al-mo ³		Al-usp ³		Al-sp ³ Ferron	Al(OH) ₃ ppt
	80	17	NMR ⁴	Ferron	NMR ²	Ferron		
NaOH/Al molar ratio = 2.2								
5	0.543	0.457	46	56	455	471	17	nil
204	0.662	0.382	54	49	375	449	62	nil
452	0.875	0.319	68	59	325	287	145	nil
1343	0.658	0.123	54	64	144	149	302	21
1294 ⁶	1.11	nil	84	76	nil	(12)	255	172
675 ⁶	1.31	nil	98	85	nil	(13)	117	301
995 ⁶	1.64	nil	120	105	nil	(10)	130	270
NaOH/Al molar ratio = 1.0								
50	3.91	0.18	272	300	195	206	19	nil
168	3.73	0.10	276	279	119	172	56	nil
221	3.76	0.14	262	284	157	182	47	nil
315	3.93	0.15	274	303	166	155	72	nil
435	4.10	0.12	285	280	138	148	76	nil
723	3.83	0.09	267	308	70	75	150	nil
840	3.79	tr	264	284	tr	76	151	nil
1060	4.1	tr	285	291	tr	67	160	nil
6 yr	3.82	nil	266	295	nil	32	209	nil
840 ⁶	4.57	nil	317	309	nil	(20)	110	96
1060 ⁶	4.42	nil	307	306	nil	(20)	121	84

¹ Total Al = 540 mg/liter. Speciation of Al ions was made using ²⁷Al nuclear magnetic resonance spectroscopy and kinetics of Al-ferron reaction.

² Nuclear magnetic resonance (NMR) intensity ratio relative to reference.

³ Al-mo = monomeric Al species; Al-usp = unstable polymeric Al species; Al-sp = stable polymeric Al species. Values in parentheses were only estimated.

⁴ Calculated from integrated area of peak at 80 ppm and Figure 1.

⁵ Calculated from integrated area of peak at 17 ppm and Figure 2.

⁶ Formation of gibbsite was triggered by addition of submicrometer gibbsite seeds.

of this peak to the Al(OH)₄⁻ reference was linearly related to the concentration of Al present and had a correlation coefficient of .9996 (Figure 1). This peak was thus used for estimating the amount of monomeric Al in solution in this study.

In the second experiment, a series of solutions, all 0.02 M in Al, having NaOH/Al molar ratios ranging from 0 to 2.5 were studied. All these solutions were investigated within 10 days after preparation. Two peaks having chemical shifts of 80 and 17 ppm from the Al(OH)₄⁻ reference were observed in the ²⁷Al NMR spectra. The intensity for the 80-ppm peak decreased whereas that for the 17-ppm peak increased with increased NaOH/Al ratio in the preparation (Table 1). The concentrations of monomeric Al estimated from the 80-ppm peak were comparable to those determined with the kinetics of Al-ferron color development. The intensity of the peak at 17 ppm was also linearly related to the amount of unstable polymers determined by Al-ferron kinetic measurement, but the slope of the regression line varied considerably among experiments. This variation probably was due to the fact that the unstable polymers were composed of more than one species but they cannot be distinguished by the kinetics of the Al-ferron reaction (Tsai and Hsu, 1984, 1985). The data from 24 analyses show a correlation coefficient of .9835

(Figure 2). For a first approximation, the relationship given in Figure 2 was used for converting the intensity of the peak at 17 ppm to the concentration of unstable OH-Al polymers for comparison. Only very small amounts of stable polymers were detected in these freshly prepared solutions based on the kinetics of the Al-ferron reaction.

In another experiment, two series of solutions having NaOH/Al molar ratio of 2.2 or 1.0, all 0.02 M in Al but aged for different durations, were investigated. Gibbsite was formed in some solutions. The gibbsite precipitate was removed by filtration through a Millipore filter paper of 0.22- μ m pore size before analysis. Table 2 shows that, with each of these two series of solutions, the concentration of monomeric Al species measured with either Al-ferron kinetics or NMR spectroscopy remained unchanged as long as little gibbsite was present. The formation of gibbsite resulted in a decrease in pH and thus a slight increase in monomeric Al ions. Al-ferron reaction kinetics also showed that the amount of unstable polymers decreased with time and completely disappeared after prolonged aging. This phenomenon was most obvious in solutions in which large amounts of gibbsite formed. This decrease in the concentration of unstable polymers was accompanied by a decrease in the peak at 17 ppm in the NMR

spectra. The concentrations of unstable polymers estimated from the 17-ppm peak and Figure 2 are comparable.

The Al-ferron reaction further showed that the amount of stable polymers gradually increased with time and became the dominant polymeric species in all aged solutions. The addition of sodium sulfate yielded a basic aluminum sulfate which was distinctly different from the precipitate obtained from fresh OH-Al solutions in their X-ray powder diffraction patterns, morphology, and reaction rates with acid, similar to the results reported by Tsai and Hsu (1984, 1985). Nevertheless, no additional peaks corresponding to the stable polymers were observed in the ^{27}Al NMR spectra of any of these solutions. Evidently the stable polymers formed during aging were not detectable by ^{27}Al NMR spectroscopy.

The Al-13 configuration consists of one AlO_4 tetrahedron at the center, surrounded by four trioctahedral OH-Al unit structures at the four corners of a truncated tetrahedron. This structure should not be stable in aqueous solution because of the following reasons: (1) Al-O is known to be unstable in aqueous medium and tends to become hydrated to Al-OH or Al-OH₂. To circumvent this difficulty, the composition was revised to $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$ or $[\text{Al}_{13}(\text{OH})_{34}]^{5+}$ in some reports (Sillen, 1959; Aveston, 1965); (2) Trioctahedral OH-Al configuration has not been observed in any stable compound; and (3) In the Al-13 configuration, 13 Al^{3+} ions are packed within 40 oxygen atoms (4 O^{2-} , 24 OH^- , and 12 H_2O). The charge density of this configuration is much higher than that in gibbsite in which 13 Al^{3+} ions are packed within 48 OH^- , and gibbsite is known to be stable in earth surface environment. On the other hand, the gibbsite-fragment model has a layer structure. A non-symmetrical species of a spin 5/2 nuclei will have short T_2 s and, therefore, are not observable in the NMR spectra. The combined ^{27}Al NMR spectroscopy and ferron kinetic studies suggests that a portion of the unstable polymers initially formed might be interpreted as a Al-13 configuration, whereas the stable polymers formed during aging might have the structure of gibbsite.

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