

ROLE OF TARTARIC ACID IN THE INHIBITION OF THE FORMATION OF Al_{13} TRIDECAMER USING SULFATE PRECIPITATION

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Abstract—Polynuclear Al_{13} tridecamer species are the major hydrolyzed species of aluminum, but their occurrence in terrestrial environments has not been established. X-ray diffraction (XRD), ^{27}Al nuclear magnetic resonance (NMR), and scanning electron microscope (SEM) analyses show that the presence of tartaric acid (concentration range of 10^{-5} – 10^{-3} M), one of the commonly occurring low-molecular-weight organic acids, inhibits the formation of the Al_{13} tridecamer species.

In the absence of tartaric acid, the basic aluminum sulfate crystals were of tetrahedral morphology and conformed to isometric symmetry with $a = 17.748 \text{ \AA}$ and space group of $P4_232$. Increasing amounts of tartaric acid [tartaric acid/Al molar ratio (R) ranging from 0.01 to 0.05] modified the crystal morphology from the tetrahedral particles of isometric symmetry ($R = 0$) to rod-shaped particles of monoclinic symmetry ($R = 0.01$) to irregularly shaped X-ray noncrystalline microparticles ($R = 0.05$). Failure to detect the presence of Al_{13} tridecamer, the dominant hydrolyzed species of aluminum, in terrestrial environments may be partially attributed to the presence of low-molecular-weight organic acids, which inhibit the formation of Al_{13} tridecamer species.

Key Words—Al-Hydroxy Sulfates, Al_{13} Tridecamer, Powder XRD Data, SEM, Solid-State NMR, Tartaric Acid.

INTRODUCTION

Aluminum is released from aluminosilicate minerals into soil solution due to acidity generated by natural and anthropogenic processes. High reactivity of Al leads to hydrolytic reactions and to strong complexation with naturally occurring organic acids commonly present in soils (Huang, 1988; Vance *et al.*, 1996). The relative distribution of the hydrolyzed and complexed Al species is the determining factor for Al mobility in soil solution and toxicity to natural ecosystems (Bertsch and Parker, 1996).

Aluminum can polymerize into various polynuclear species. From crystallographic data of basic aluminum sulfates precipitated from Al-OH solutions, the Al_{13} polycation (hereafter referred to as 'tridecamer'), with the idealized formula of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, is the dominant hydrolyzed species formed from the hydrolysis of Al^{3+} at an OH/Al molar ratio of ~ 2.5 (Johansson, 1960). The existence of Al_{13} tridecamer was later confirmed in Al-OH solutions by a number of investigations employing ^{27}Al and ^{17}O nuclear magnetic resonance spectroscopy (NMR) (Akitt *et al.*, 1972; Bottero *et al.*, 1980; Akitt and Farthing, 1981; Bertsch *et al.*, 1986a, 1986b; Bertsch, 1987; Thompson *et al.*, 1987; Akitt and Elders, 1988; Akitt, 1989). The Al_{13} tridecamer is probably a type of "Keggin" structure, consisting of a symmetrical, cage-like arrangement of 12 octahedrally coordinated Al atoms

surrounding a single tetrahedral core atom (Bartlett and Riego, 1972; Akitt and Farthing, 1981). The ^{27}Al NMR resonance of the AlO_4 nucleus of the Al_{13} tridecamer is observed at 62.5 ppm in solution (Akitt and Elders, 1988) and also at a near identical position for sulfate crystals (Mueller *et al.*, 1981; Kunwar *et al.*, 1984).

Direct ^{27}Al NMR evidence of the Al_{13} tridecamer in two organic forest soil horizons of Camel's Hump State Forest in Vermont, USA was recently obtained (Hunter and Ross, 1991). However, subsequent NMR investigations of many soil samples, including the re-sampling of the Camel's Hump sites, failed to reveal any indication of Al_{13} tridecamer, although the presence of the Al_{13} polycation may be masked by other paramagnetic metals (*e.g.*, Fe, Mn) in these soils (Bertsch and Parker, 1996). The Al_{13} tridecamer is ten-fold more toxic to plants than the hexaquo Al ion (Parker *et al.*, 1989), suggesting the importance of the study on the formation and transformation of Al_{13} tridecamer in natural ecosystems.

Since basic aluminum sulfate precipitates and the original OH-Al polymers in solution appear to be the same, as observed from the identical chemical shift of 62.5 ppm in both systems (Mueller *et al.*, 1981; Kunwar *et al.*, 1984), an understanding of the basic aluminum sulfate precipitates formed under the influence of ionic environments similar to those encountered in natural ecosystems may provide important information on the original OH-Al polymers in solution. Here we present ^{27}Al NMR, scanning electron microscope (SEM) and X-ray diffraction (XRD) evidence showing that the presence of tartaric acid strongly perturbs the

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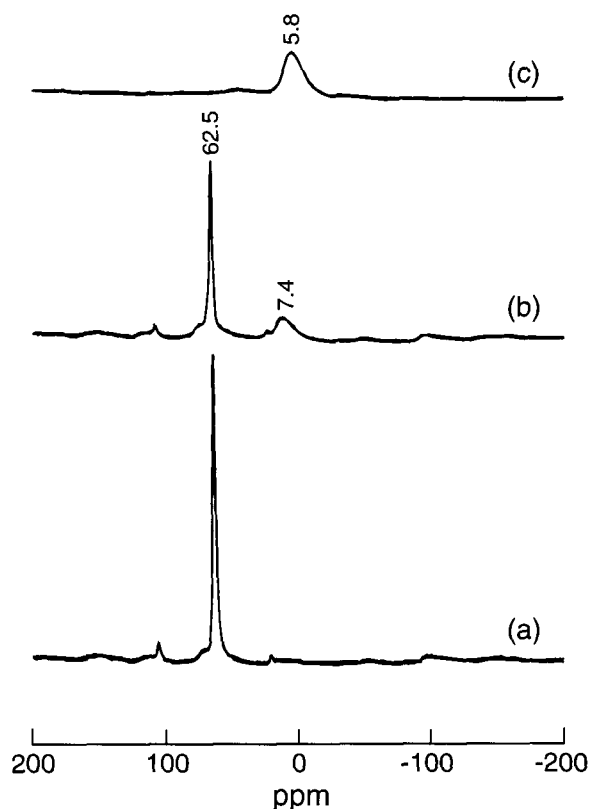


Figure 1. ^{27}Al NMR spectra of the basic aluminum sulfates precipitate after aging for 12 d, from OH-Al solutions aged for 5 d, and formed at pH 4.53 and different tartaric acid/Al molar ratios (R). (a) Control at R = 0; (b) Sample at R = 0.01; (c) Sample at R = 0.05.

crystallization of basic aluminum sulfate precipitates formed from the OH-Al solutions hydrolyzed at pH 4.53, and inhibits the formation of Al_{13} tridecamer. This perturbation effect of tartaric acid, one of the low-molecular-weight organic acids commonly occurring in terrestrial ecosystems, partially explains the fact that the occurrence of Al_{13} tridecamer species in natural soils has never been established.

MATERIALS AND METHODS

Preparation of OH-Al solutions

Solutions with an OH/Al molar ratio of 2.2 were prepared by titrating 100 mL of 0.1 M $AlCl_3$ solution to pH 4.53 with 0.1 M NaOH at a rate of 1 mL per min; the solution was diluted to 500 mL. The final concentration of Al in the solution was 0.02 M. The solution ^{27}Al NMR spectra show that Al was present as an Al_{13} species (chemical shift of 62.5 ppm) (data not shown). Hydroxy-Al solutions titrated to pH 4.53, at the tartaric acid/Al molar ratios (R) of 0.01 and 0.05 (concentration of tartaric acid ranging from 2×10^{-4} to 1×10^{-3} M), were also prepared as described above.

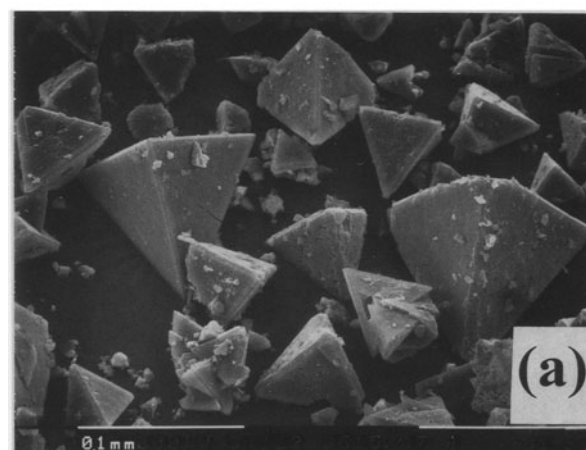
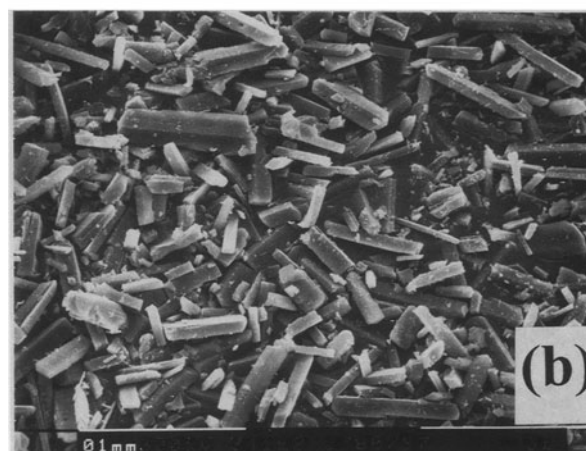
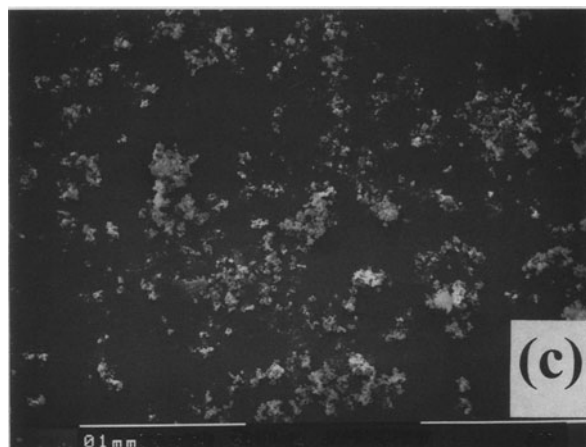


Figure 2. SEM photographs of the basic aluminum sulfates precipitate after aging for 12 d, from OH-Al solutions aged for 5 d, and formed at pH 4.53 and different tartaric acid/Al molar ratios (R). (a) Control at R = 0; (b) Sample at R = 0.01; (c) Sample at R = 0.05. Scale = 0.1 mm.

Table 1. XRD data of the basic aluminum sulfate crystals of tetrahedral habit formed from hydroxy-Al solutions (pH 4.53), together with the data of earlier reports.

Present work		Calculated ¹		Johansson <i>et al.</i> (1960) ²		Bassett and Goodwin (1949) ³		Bersillon <i>et al.</i> (1980) ³		Tsai and Hsu (1984) ³	
<i>d</i> (Å)	l	<i>d</i> (Å)	<i>hkl</i>	<i>d</i> (Å)	<i>hkl</i>	<i>d</i> (Å)	l	<i>d</i> (Å)	l	<i>d</i> (Å)	l
10.24	6	10.25	111	10.33	111	12.15	10	12.30	10	12.20	2
						9.89	9	10.00	6	10.40	10
8.87	3	8.87	200	8.95	200			9.61	1		
						8.77	6	8.85	2	8.93	7
						7.00	3	6.93	2		
5.129	10	5.123	222	5.167	222	5.88	4	5.83	1	6.53	1
						5.25	3			5.83	1
4.442	2	4.437	400	4.475	400	4.45	7	4.58	3	4.47	3
								4.37	3		
4.069	1	4.072	331	4.106	331	4.12	6	4.17	3	4.10	2
						3.80	5	4.06	2		
3.620	2	3.623	422	3.654	422			3.83	1	3.65	4
						3.56	5	3.53	1		
3.417	6	3.416	333,511	3.445	333,511	3.29	5	3.33	1	3.44	10
								3.24	1		
3.139	2	3.137	440	3.164	440	3.15	2				
3.002	2	3.000	531	3.026	531	3.01	4	3.00	1	3.02	3
						2.86	3	2.86	1	2.82	1
2.678	2	2.676	622	2.698	622	2.67	6	2.65	2	2.69	6
2.562	3	2.562	444	2.584	444	2.43	2	2.39	1	2.57	4
								2.30	1	2.38	1
2.312	1	2.312	731	2.330	731			2.20	1	2.32	2
2.221	2	2.218	800	2.238	800			2.20	1	2.23	3
2.092	1	2.092	822	2.109	822			2.12	2	2.10	1
1.947	2	1.948	911,753	1.965	911,753			1.92	2	1.96	3
1.783	1	1.784	771	1.799	711						
1.569	1	1.569	880	1.582	880						

¹ From present work, isometric, $a = 17.748 \pm 0.003$ Å.

² Calculated in the present study from the single crystal data.

³ Powder XRD data.

Precipitation of basic aluminum sulfates

Fifty milliliters of 0.5 M sodium sulfate was mixed with 200 mL of the OH-Al solution formed both in the absence and presence of tartaric acid at $R = 0.01$ and 0.05 , and pre-aged for 5 d to make the final concentration of 0.016 M Al and 0.1 M sulfate. The precipitate of the basic aluminum sulfate, formed from the solution aged for 12 d, was collected by ultrafiltration using a 0.01 μm nitro-cellulose filter.

Analysis of the aluminum sulfate precipitates

High resolution solid-state NMR spectra were obtained at ambient temperature ($\sim 23^\circ\text{C}$) on a Bruker AM360WB spectrometer with a CP/MAS accessory using 80 Hz line broadening, with 90° pulse of 6.5 μs and recycle delay of 1 s, and a spinning speed of 4 KHz, with AlCl_3 chemical as a reference. The morphology of the precipitates was examined using a Philips 505 SEM operating at 30 kV. The precipitation products were examined by XRD using $\text{FeK}\alpha$ radiation on a Rigaku Rotaflex 2000 X-ray diffractometer

equipped with graphite monochromator, operating at 40 kV and 130 mA at a step-scan rate of 0.01 °/2θ per s.

RESULTS AND DISCUSSION

Absence of tartaric acid

The ^{27}Al NMR spectrum of the sulfate precipitates formed in the absence of tartaric acid ($R = 0$) shows only one strong resonance peak at 62.5 ppm (Figure 1). The Al_{13} tridecamer $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ gives two resonances, a sharp one at 62.5 ppm from the AlO_4 nucleus and which is always visible, and a very broad one from the 12 octahedrally coordinated Al atoms at ~ 12 ppm (Akitt, 1989). At room temperature, only the AlO_4 resonance at 62.5 ppm is observed, and the octahedral component is only visible if the solution is heated (Akitt and Farthing, 1981). The presence of a single peak at a chemical shift of 62.5 ppm indicates the presence of an Al_{13} tridecamer in the precipitates. Previous studies (Bottero *et al.*, 1980, 1982; Akitt and Farthing, 1981) showed that at an OH/Al molar ratio of 2.2 , the Al_{13} tridecamer spe-

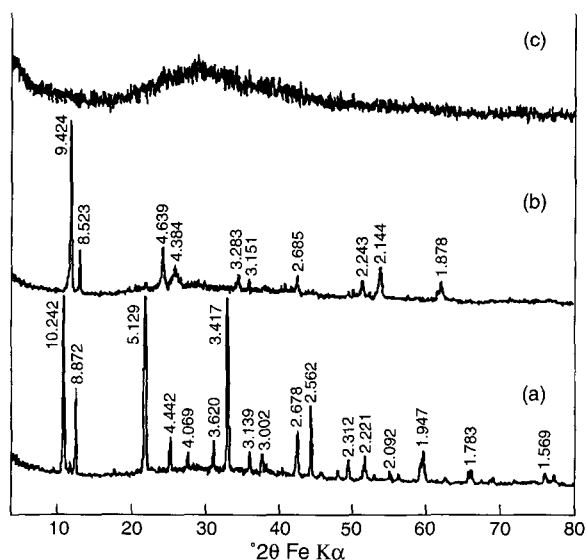


Figure 3. XRD patterns of the basic aluminum sulfates precipitate after aging for 12 d, from OH-Al solutions aged for 5 d, and formed at pH 4.53 and different tartaric acid/Al molar ratios (R). (a) Control at R = 0; (b) Sample at R = 0.01; (c) Sample at R = 0.05.

cies represent nearly all of the Al present in the hydrolyzed form. Recently, Masion *et al.* (1994) confirmed from a quantitative decomposition of liquid NMR spectra that 93% of total Al was involved in the Al₁₃ tridecamer. Note also that the chemical shifts observed in the solid-state NMR spectra are only apparent shifts, because of the second-order quadrupole interactions.

The SEM images (Figure 2) of the aluminum sulfate precipitates indicate that the precipitates are homogeneous crystals of tetrahedral habit, with edges averaging 0.07 mm long (Figure 2a). Crystals of no other habit were observed in the precipitates, contrary to the findings of Tsai and Hsu (1984, 1985) who obtained crystals of three different habits *viz.*, tetrahedral, spherical, and irregular habit.

The powder XRD pattern of the precipitate with tetrahedral habit (Table 1; Figure 3a) was distinctly different from the powder XRD patterns of the other forms of basic aluminum sulfates reported (*e.g.*, Bassett and Goodwin, 1949; Hollingsworth and Bannister, 1950; Brydon and Singh, 1969; Bersillon *et al.*, 1980; Tsai and Hsu, 1984). The powder XRD pattern was indexed following the method outlined by Azaroff and Buerger (1958) and the unit-cell dimensions were refined using the non-linear *least-squares* refinement program UNITCELL (Holland and Redfern, 1997). The crystals are isometric ($a = 17.748(3)$ Å) and space group $P4_232$ was based on the systematic conditions for reflections observed in the powder XRD pattern (Figure 3a). There was good agreement between the d -values calculated from the unit-cell dimensions and

Table 2. XRD data of the platy rod-shaped basic aluminum sulfate crystals formed from hydroxy-Al solutions (pH 4.53) in the presence of tartaric acid (R = 0.01).

Present work		Calculated ¹	
d (Å)	l	d (Å)	hkl
9.42	10	9.58	011
8.52	3	8.66	002
4.639	3	4.72	301
4.384	2	4.56	113
3.283	1	3.36	204
3.151	1	3.20	105
2.685	2	2.74	503
2.243	1	2.25	604
2.144	3	2.16	008
1.878	2	1.88	604

¹ Calculated in the present study from the single crystal data of Johansson (1962): Monoclinic: $a = 14.18$, $b = 11.50$, $c = 17.73$ Å, and $\beta = 102.3^\circ$.

those observed in the powder XRD pattern (Table 1). The unit-cell dimension of $17.748(3)$ Å calculated from the powder XRD data in the present study is in good agreement with that reported for tetrahedral single crystals of basic aluminum sulfates obtained from Al-OH solutions at Al concentration of 0.01–0.1 M and an OH/Al molar ratio of 2.5, using X-ray Weissenberg photographs ($a = 17.9(1)$ Å, Johansson *et al.*, 1960). Based on the single crystal data of Johansson *et al.* (1960), the d -values were calculated in the present study and are also included in Table 1.

Presence of tartaric acid

Tartaric acid, at R = 0.01, modified the crystallization processes such that platy rod-shaped particles formed (Figure 2b). The d -values obtained from the powder XRD pattern (Figure 3b) of the platy rod-shaped particles formed in the presence of tartaric acid (R = 0.01) at an OH/Al molar ratio of 2.2 (the present study) matched closely the d -values we calculated from the unit-cell dimensions of the single crystal, formed in the absence of tartaric acid (R = 0) and at the Al concentration of 0.25 M and at an OH/Al molar ratio of 2.5, reported by Johansson (1962) (Table 2). Johansson (1962) did not present the powder XRD data of the crystal. He reported that the single crystals conform to monoclinic symmetry with $a = 14.18$ Å, $b = 11.50$ Å, $c = 17.73$ Å, and $\beta = 102.3^\circ$ and space group of $P2_1/n$ from single crystal data. Hence, we conclude that the rod-shaped crystals of aluminum sulfate precipitates formed at R = 0.01 in the present study conform to monoclinic symmetry.

The presence of tartaric acid at R = 0.01 appeared to suppress the formation of Al₁₃ tridecamer species (resonance at 62.5 ppm) and promote the formation of octahedral Al species (broad peak around 7.4 ppm), probably complexed with the organic acid (Figure 1b). Further increase of the concentration of tartaric acid

($R = 0.05$) inhibited the formation of Al_{13} tridecamer species as indicated by the absence of the resonance at 62.5 ppm (due to Al_{13} tridecamer) and the presence of a strong broad peak around 5.8 ppm (octahedral Al-tartrate complex) in the ^{27}Al NMR spectrum (Figure 1c). The crystallization processes involving the precipitated aluminum sulfates were perturbed by tartrate, producing (X-ray) amorphous products (Figure 3c). The morphology of the particles was also modified from the tetrahedral particles ($R = 0$) to rod-shaped particles ($R = 0.01$) to irregularly shaped microparticles ($R = 0.05$) (Figure 2c).

Concentrations of organic acid under terrestrial ecosystems may range from 10^{-3} to 10^{-5} M (Robert and Berthelin, 1986). However, higher concentrations ($>10^{-3}$ M) are localized in the soil rhizosphere and under litter in contact with living organisms. Under aerobic conditions, oxalic, citric, tartaric, and malic acids are dominant, whereas in anaerobic conditions, volatile acids predominate. The present study shows that Al_{13} tridecamer, the dominant hydrolyzed species of aluminum, is below detection in natural terrestrial environments at least partially because low-molecular-weight organic acids, as illustrated by tartaric acid, suppress the formation of Al_{13} tridecamer species. Although recent reports showed that the Al_{13} tridecamer ion is ten-fold more toxic to plants than the hexaquo Al ion (Parker *et al.*, 1989), the results reported in the present study indicate that organic acids, such as tartaric acid, inhibit the formation of Al_{13} tridecamer ion thereby alleviating Al toxicity.

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