

## INFLUENCE OF ACETATE, OXALATE, AND CITRATE ANIONS ON PRECIPITATION OF ALUMINUM HYDROXIDE

**Key Words**—Acetate, Aluminum hydroxide, Carboxylic acid, Citrate, Oxalate, Precipitation.

### INTRODUCTION

Huang and Keller (1972) and Lind and Hem (1975) reported that polybasic acids are important in the development and weathering of soil due to their ability to complex and solubilize aluminum. In addition, the edge faces of synthetic goethite (Parfitt *et al.*, 1977a) and gibbsite (Parfitt *et al.*, 1977b) can adsorb oxalate. Ng Kee Kwong and Huang (1975, 1977, 1978) showed that the hydrolysis of aluminum chloride to form gibbsite is inhibited by citrate. Complex formation with organic ligands slows the rate of crystallization of aluminum hydroxide and influences the polymorphic form of the final crystalline product (Violante and Violante, 1980).

Fulvic and humic acids in soil may influence the dissolution and reprecipitation of aluminum resulting from rock and mineral decomposition. Polybasic acids react with aluminum, forming complexes which alter the process of precipitation of aluminum hydroxide or iron(III) hydroxide by retarding crystallization and by facilitating the formation of intermediate materials (Schwertmann *et al.*, 1968; Schwertmann, 1970; Fischer and Schwertmann, 1975). These acids have also been shown to aid in the crystallization of kaolinite from an aluminum silicate solution (Lind and Hem, 1975).

The interaction of polybasic acids with aluminum is also of interest because the salts of these acids are often used in (1) the extraction and determination of exchangeable cation (ammonium acetate) and (2) the extraction of aluminum and iron

from non- or poorly crystalline phases in soils (oxalate and citrate salts). In addition, the citrate anion is also used to adjust the viscosity of clay suspensions and aluminum hydroxide gels.

In the present study, the effect of mono-, di-, and tribasic carboxylic acids on the precipitation of aluminum hydroxide was examined and related to the dissolution and reprecipitation of aluminum, processes that may take place in soil solutions during weathering.

### EXPERIMENTAL

#### Potentiometric titration

Twenty milliliters of 0.1 M  $AlCl_3$  was titrated with 0.1 N NaOH or 0.1 M  $Na_2CO_3$ . Prior to titration, an appropriate quantity of potassium acetate, oxalate, or citrate was dissolved in the  $AlCl_3$  to produce various molar ratios of anion to aluminum. Because similar results were obtained with 0.1 N NaOH and 0.1 M  $Na_2CO_3$ , only the titrations with 0.1 N NaOH will be presented.

#### Chemical analysis

The precipitates were washed with water by centrifuging at 15,000 rpm ( $27,000 \times g$ ) for 30 min until the filtrate was free of chloride ion and then dried in a vacuum desiccator containing phosphorus pentoxide and silica gel. The precipitates were analyzed for oxalate or citrate by the Walkley-Black method for organic carbon (Walkley and Black, 1934) and the results expressed as the molar ratio of anion to aluminum. The hydroxyl ion content of the precipitates was determined by the modified sodium fluoride method (Hsu, 1966) and expressed as the molar ratio of hydroxyl to aluminum. The aluminum content was determined by chelatometric titration (United States Pharmacopoeia, 1980).

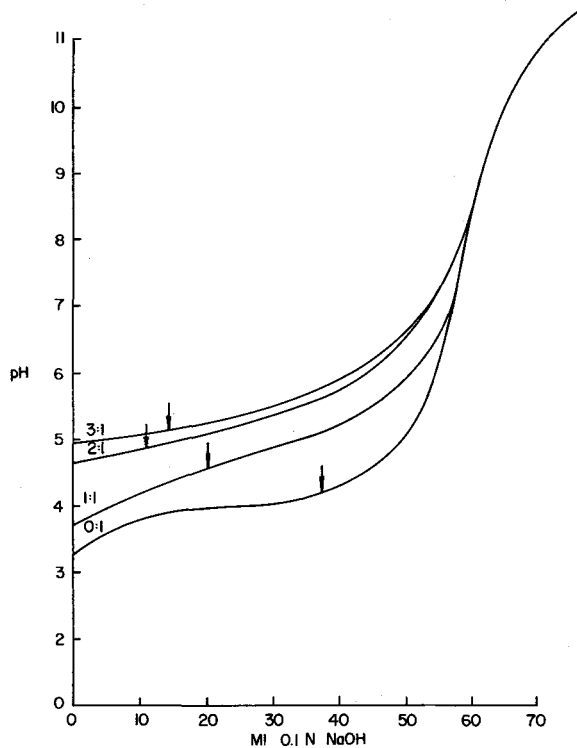


Figure 1. Effect of KOAc on the potentiometric titration of 0.1 M  $AlCl_3$  by 0.1 N NaOH. Molar ratio of acetate to aluminum was 0, 1.0, 2.0, or 3.0. ↓ = appearance of visible precipitation.

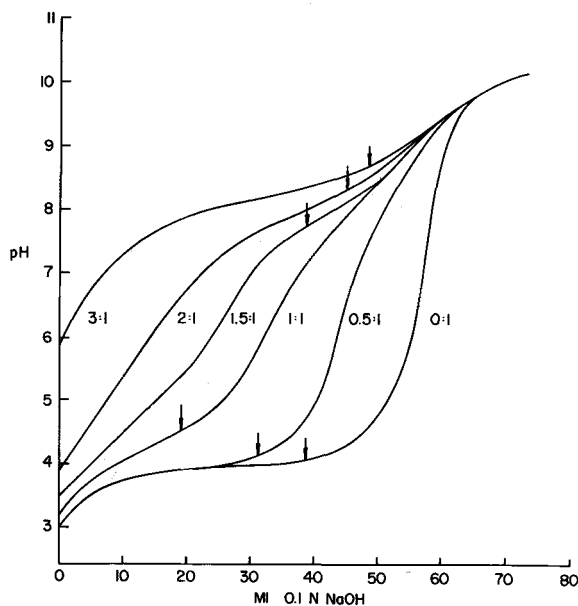


Figure 2. Effect of K oxalate on the potentiometric titration of 0.1 M  $AlCl_3$  by 0.1 N NaOH. Molar ratio of oxalate to aluminum was 0, 0.5, 1, 1.5, 2.0, or 3.0. ↓ = appearance of visible precipitation.

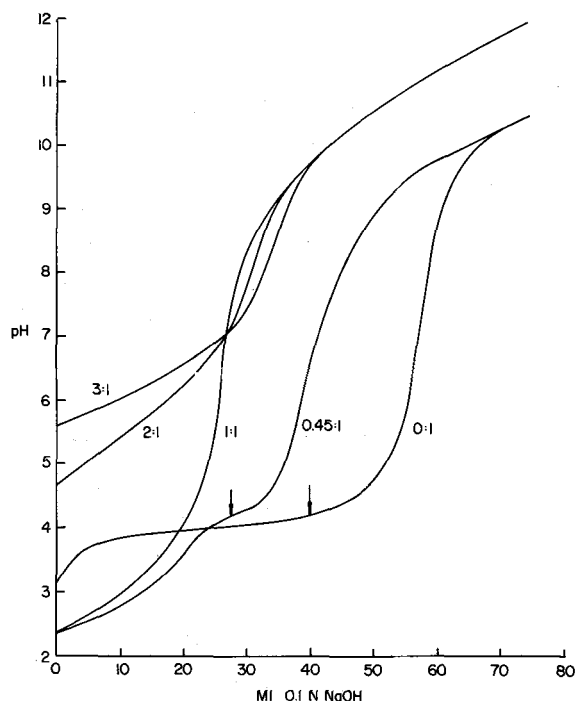


Figure 3. Effect of K citrate on the potentiometric titration of 0.1 M  $\text{AlCl}_3$  by 0.1 N NaOH. Molar ratio of citrate to aluminum was 0, 0.45, 1.0, 2.0, or 3.0.  $\downarrow$  = appearance of visible precipitation.

#### Infrared analysis

Infrared analysis (Perkin-Elmer 180 spectrophotometer) of the soluble complexes was performed by stopping the titration 0.5 pH units before the previously determined pH of precipitation and air drying a portion of the solution on AgCl windows or by preparing KBr pellets of the air-dried powders.

#### X-ray powder diffraction

Dried samples of the soluble complexes were obtained as above. X-ray powder diffractograms of random powder samples mounted in McCreery holders were recorded on a Siemens X-ray diffractometer using  $\text{CuK}\alpha$  radiation.

### RESULTS AND DISCUSSION

The titration curves of  $\text{AlCl}_3$  in the presence of various molar ratios of KOAc, K-oxalate or K-citrate using 0.1 N NaOH as the titrant are shown in Figures 1–3. Similar results were obtained using 0.1 M  $\text{Na}_2\text{CO}_3$ . KOAc had little effect on the titration of  $\text{AlCl}_3$ , except to shift the titration curve to slightly higher pHs and to increase the pH at which a precipitate was first observed (Figure 1). Based on the increase of the pH of

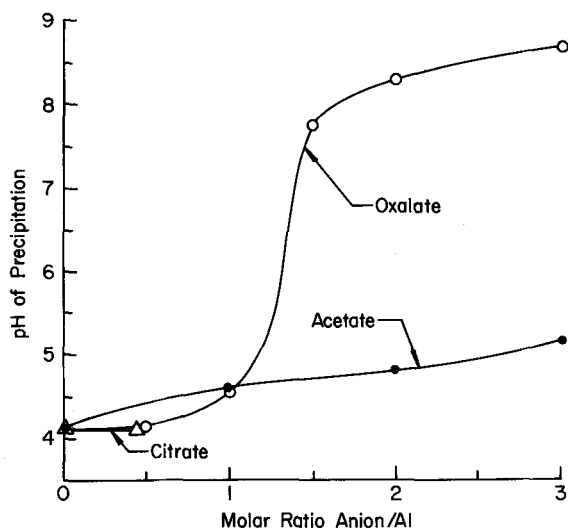


Figure 4. Effect of (●) acetate, (○) oxalate, and (△) citrate on the pH of visible precipitation of aluminum hydroxide during the titration of 0.1 M  $\text{AlCl}_3$  by 0.1 N NaOH.

precipitation with acetate concentration, acetate appears to compete with hydroxyl for bonding to aluminum (Figure 4).

Oxalate anion appears to interact more strongly with aluminum as evidenced by the shape of the titration curve of aluminum chloride and the pH at which precipitation occurred (Figure 2). The pH was higher for the same concentration of NaOH in the presence of oxalate anion than for acetate anion. For example, the pH was 3.7 after the addition of 30 ml of 0.1 N NaOH in the absence of oxalate but was 5.5 and 8.2 in the presence of 1:1 or 3:1 oxalate to aluminum, respectively. Comparable pH values in the presence of acetate anion were 4.7 and 5.2. The added hydroxyls apparently affected the pH more strongly as oxalate occupied the aluminum bonding sites. A very sharp increase in the pH of precipitation occurred between 1:1 and 2:1 oxalate to aluminum (Figure 4) indicating that very high concentrations of hydroxyl ions were necessary in the presence of oxalate.

Chemical analysis of the precipitate formed in the presence of 1:1 oxalate to aluminum (Table 1) showed that the oxalate concentration remained constant between pH 5 and 7, but decreased at pH 9. Little increase was seen in the oxalate content of the precipitate at pH 9 when the oxalate to aluminum ratio during the titration was increased to 2:1 or 3:1.

As a result of infrared studies, Fujita *et al.* (1962) proposed that the oxalate-metal complexes might exist as  $\text{C}_{2v}$ ,  $\text{V}_{11}$ , or  $\text{D}_3$  structures. A high degree of occupancy of the six aluminum sites coordinated by oxalate apparently inhibits the replacement of oxalate by hydroxyl, thus requiring a high concentration of hydroxyl to initiate the precipitation. Citrate anion had the greatest effect on the titration of  $\text{AlCl}_3$  (Figure 3). As noted

Table 1. Composition of aluminum hydroxide precipitated in the presence of potassium oxalate or potassium citrate.

Complexing anion	Complexing anion aluminum molar ratio during titration	Composition of precipitate at pH expressed as molar ratio					
		5		7		9	
		Anion/Al	OH/Al	Anion/Al	OH/Al	Anion/Al	OH/Al
Oxalate	1:1	0.44	1.94	0.48	2.25	0.15	2.57
	2:1	—	—	—	—	0.25	2.74
	3:1	—	—	—	—	0.21	2.59
Citrate	0.4:1	0.21	1.10	0.21	1.09	0.21	1:12

in Figure 4, when the molar ratio of citrate to aluminum was 0.45 or less, precipitation occurred at about the same pH as the control. At a molar ratio of citrate to aluminum between 0.475 and 3.0, no precipitate was observed even at pH 12, indicating that hydroxyl can not replace citrate at this relative concentration and that a soluble aluminum complex exists at molar ratios of citrate to aluminum above 0.475.

Chemical analysis of the precipitate formed in the presence of a 0.40 molar ratio of citrate to aluminum in the range of pH 5 to 9 also shows that hydroxyl can not replace citrate because the citrate and hydroxyl concentrations remained constant at pH 5, 7, and 9 (Table 1). The presence of citrate anion, because of its strong complexation of aluminum and/or its competitive ability compared to hydroxyl and fluoride anions, may result in the measured hydroxyl values being less than their true value. Regardless of the actual value, the hydroxyl concentration remained constant between pH 5 and 9.

On the basis of the pH of precipitation, it appears that the strength of the aluminum-anion bond is in the order: citrate > oxalate > acetate. Thus, acetate can be most easily replaced by hydroxyl to form aluminum hydroxide. Replacement of the oxalate anion in the aluminum oxalate complex by hydroxyl is dependent on the molar ratio of oxalate to aluminum. With an increase in the molar ratio of oxalate to aluminum from 1 to 1.5, the hydroxyl ion concentration must be increased approximately 1000 times in order for the hydroxyl ions to replace oxalate and thus allow the formation of basic aluminum oxalate.

The soluble complex formed in the presence of a molar ratio of 3 oxalate to aluminum is believed to be the aluminum oxalate complex identified by Fujita *et al.* (1962), on the basis of the similarity of the infrared spectra (Table 2). Upon air drying the soluble complex produced a crystalline powder (Table 3).

Citrate formed a stable complex with aluminum and completely blocked the precipitation of aluminum hydroxide at citrate to aluminum ratios greater than 0.475. The infrared spectrum of an air-dried sample of 1:1 citrate to aluminum complex (Table 4) is very similar to the infrared spectrum of commercial aluminum citrate. The structure of the complex indicated by the infrared spectrum is consistent with the studies of Lind and Hem (1975) who reported that the carboxylate groups were involved in aluminum complexes, but not alcoholic hydroxyl groups. The dried samples of the soluble complexes from the titration of aluminum chloride in the presence of all molar ratios of citrate to aluminum (Figure 3) were amorphous to X-rays.

### CONCLUSIONS

The results suggest that citrate extraction of noncrystalline aluminum hydroxide phases from soils must be carried out with citrate concentrations such that the citrate/aluminum molar

Table 2. Infrared frequencies of air-dried soluble complex formed in the presence of 3:1 molar ratio of oxalate to aluminum.

Wave number (cm <sup>-1</sup> )		
Soluble complex	K <sub>2</sub> (AlOx <sub>3</sub> ) <sup>1</sup>	Assignment <sup>1</sup>
1720	1722	$\nu_a(\text{C}=\text{O})$
1695	1700 1683	$\nu_a(\text{C}=\text{O})$
1660		
1640	1405	$\nu_s(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$
1403		
1460	1292 1269	$\nu_s(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$
1295		
1270	—	
1180	—	
1105	—	
1025	—	
910	904	$\nu_s(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$
818	820	$\delta(\text{O}-\text{C}=\text{O}) + \nu(\text{M}-\text{O})$
	803	
640	—	
583	587	$\nu(\text{M}-\text{O}) + \nu(\text{C}-\text{C})$
478	436	ring deformation + $\delta(\text{O}-\text{C}=\text{O})$

<sup>1</sup> Fujita *et al.* (1962).

ratio is greater than 0.475. This condition is normally met because most procedures for citrate extraction of aluminum and iron specify 0.2 M or 0.3 M Na-citrate solutions.

The results also suggest that acetate solutions, such as ammonium acetate solution which is sometimes used for replacing exchangeable cations in soils, should be used with caution because the high operational pH range of this acetate salt inhibits extraction of exchangeable aluminum and/or causes hydroxyl aluminum polymers to be precipitated on soil surfaces.

The concentrations of organic acids used in this study are higher than would be encountered under natural conditions; however, much more significant than the concentration of the acids is the molar ratio of anion to aluminum; the ratios in this study ranged from 0:1 to 3:1. It is instructive to compare the anion to aluminum molar ratios from data on the extraction of mineral and soil systems reported in the literature (Table 5). These ratios have been calculated using the amount of aluminum dissolved by the organic acid as the concentration of aluminum. The ratios encountered in the dissolution of aluminum in soil minerals by humic and fulvic acids range from

Table 3. X-ray powder diffraction pattern of air-dried soluble complex formed in the presence of 3:1 molar ratio of oxalate to aluminum.

d (Å)	I/I <sub>0</sub>	d (Å)	I/I <sub>0</sub>	d (Å)	I/I <sub>0</sub>
5.79	2	3.21	1	2.16	7
5.68	7	3.14	100	2.07	2
5.31	4	3.08	7	2.05	7
5.12	4	3.07	7	1.94	4
4.82	2	2.82	5	1.91	1
4.67	2	2.73	3	1.90	2
4.35	10	2.66	4	1.82	12
4.21	4	2.64	9	1.77	4
3.88	11	2.44	6	1.65	2
3.74	15	2.34	9	1.57	7
3.63	12	2.31	2	1.55	2
3.51	15	2.23	44	1.53	2
3.45	15	2.19	7		

Table 4. Infrared frequencies of air-dried soluble complex formed in the presence of 1:1 molar ratio of citrate to aluminum.

Wave number (cm <sup>-1</sup> )			
Soluble complex	Aluminum citrate <sup>1</sup>	Assignment	
1740	1725	$\nu_a(\text{C}=\text{O})$	
1630	1641	} $\nu_a(\text{C}=\text{O})$	
	1630		
1465	1470	$\nu_s(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$	
1398	1395		
1315	—		
1260	1265	} $\nu_s(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$	
1200	1215		
1155	} 1117		
1095			
1071	1075		
1030	—		
1019	—		
950	—		
910	905	$\nu_s(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$	
868	855		
790	820	} $\delta(\text{O}-\text{C}=\text{O}) + \nu(\text{M}-\text{O})$	
	787		
665	} 675		
645			
620	600		
539	} 560	$\nu(\text{M}-\text{O}) + \nu(\text{C}-\text{C})$	
530			} 520
521			
460	460	ring deformation + $\delta(\text{O}-\text{C}=\text{O})$	

<sup>1</sup> Obtained from Pfaltz and Bauer, Inc., Stamford, Connecticut.

1:1 to 19:1. For some examples of the extraction of aluminum from soils by oxalate and citrate solutions, the ratios range from 1:1 to 65:1. Thus, the anion to aluminum ratios used in this study are equal to or lower than those likely to be encountered under natural conditions and are smaller than those commonly used for oxalate and citrate extracting solutions.

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Table 5. Anion to aluminum ratio of systems used to extract aluminum from minerals and soils.

Extractant	Aluminum extracted (moles)	Anion to aluminum molar ratio
$2.9 \times 10^{-3}$ M Fulvic acid <sup>1</sup>	$1.5\text{--}8.8 \times 10^{-4}$	3:1 to 19:1
$1.2 \times 10^{-3}$ M Humic acid <sup>1</sup>	$1.5\text{--}8.8 \times 10^{-4}$	1:1 to 8:1
$2 \times 10^{-1}$ M Sodium oxalate <sup>2</sup>	$4.6 \times 10^{-3}\text{--}2.1 \times 10^{-1}$	1:1 to 43:1
$3 \times 10^{-1}$ M Sodium citrate <sup>2</sup>	$4.6 \times 10^{-3}\text{--}2.1 \times 10^{-1}$	1:1 to 65:1

<sup>1</sup> Kodama and Schnitzer (1973).

<sup>2</sup> McKeaque and Day (1966).

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