

INTERACTIONS OF CITRIC ACID AND SYNTHETIC HYDROXY-ALUMINUM MONTMORILLONITE

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Abstract—Hydroxy-Al-montmorillonite was prepared by mixing Na-Wyoming montmorillonite with $\text{Al}(\text{OH})_{2.5}$ polycations and aging the mixture for 10 days. The reactions of this complex with citric acid at millimolar concentrations were investigated at different pHs for a 4-hr reaction time. The citrate sorption data, X-ray powder diffraction patterns of the montmorillonite adsorbent, and solubility products for $\text{Al}(\text{OH})_3$, estimated after computer speciation of the aqueous solution phase, suggested two reaction mechanisms, depending on pH. At $4 < \text{pH} < 5.5$, the complex was stable, and only external hydroxy-Al polycations could react with citrate, yielding a sorption envelope characteristic of an acid having a low pK_a . At higher pH, and particularly at $\text{pH} > 7$, the interlayer Al-polymers became accessible to the ligand and desorbed quickly from the montmorillonite basal planes to form a new, external, X-ray-amorphous solid phase with citrate. This reaction produced a large second peak in the sorption envelopes near pH 8, which was controlled by the increasingly negative surface charge at high pH and by the initial concentration of citric acid. This ligand accelerated, i.e., favored kinetically, the dissociation of adsorbed hydroxy-Al polymers from montmorillonite at $\text{pH} > 7$.

Key Words—Adsorption, Citric acid, Hydroxy-Al, Montmorillonite, X-ray powder diffraction.

Résumé—On prépare une smectite hydroxyalumineuse en mélangeant et en laissant en suspension 10 jours une montmorillonite du Wyoming Na et des polycations $\text{Al}(\text{OH})_{2.5}$. Les réactions de ce complexe avec l'acide citrique en concentration millimolaire et à différent pH sont analysées à partir des quantités de citrate adsorbé, de la diffraction X appliquée à des dépôts orientés de l'argile ayant réagi, du calcul du produit de solubilité $\text{Al}(\text{OH})_3$ et des concentrations des diverses espèces en solution. Deux mécanismes sont invoqués selon les domaines de pH. A $4 < \text{pH} < 5.5$, le complexe est stable et seuls les polymères d'Al des surfaces externes peuvent réagir avec le citrate, conduisant à une fixation de citrate faible, caractérisée par des courbes en fonction du pH avec un maximum apparent. A pH plus élevé et surtout à $\text{pH} \geq 7$, tous les polymères d'Al deviennent accessibles au ligand, et sont rapidement détachés des surfaces basales pour former avec le citrate une nouvelle phase amorphe en dehors des feuillets de l'argile. Cette dernière réaction se traduit par un deuxième maximum plus important dans les courbes enveloppes, vers pH 8, dont l'amplitude est limitée par l'effet de l'augmentation des charges négatives à pH élevé, et par la quantité initiale de citrate. Cet anion accélère la dissociation des polymères d'Al et de la montmorillonite à $\text{pH} \geq 7$.

INTRODUCTION

The nature and genesis of hydroxy-aluminum smectite have been of considerable interest both in soil science and in surface chemistry (Sawhney, 1960; Brydon and Kodama, 1966; Rich, 1968; Brown and Newman, 1973; Veith, 1978; Brindley and Kao, 1980; Harsh and Doner, 1985). In particular, the structure of the interlayer hydroxy-Al polymers (Hsu, 1968; Veith, 1977; Lahav *et al.*, 1978; Plee *et al.*, 1985) and their adsorption reactions with anions (Webber and Clark, 1969; Singh and Brydon, 1970; Keren and Gast, 1983; Goh and Huang, 1984; Harsh and Doner, 1985) have been examined in relation to anion solubility (Traina *et al.*, 1987) or Al toxicity (Goh *et al.*, 1986). Huang and Violante (1986) summarized research on the influence

of organic acids on the genesis of hydroxy-Al montmorillonite under conditions similar to those in acidic surface soils that contain significant amounts of labile organic matter. Experiments with synthetic, Al-complexing organic ligands, such as citric or tannic acid, show that these ligands can perturb the formation of hydroxy-Al montmorillonite in the acidic pH range. The purpose of the present study was to investigate the reactions of previously formed hydroxy-Al montmorillonite with citric acid at environmentally significant concentrations (≤ 1 mmole/liter) and at $4 < \text{pH} < 9$.

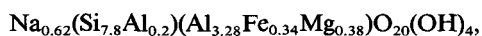
Hsu (1968), Brown and Newman (1973), and Veith (1978) pointed out that the most stable hydroxy-Al polymers between smectite layers exhibit an OH/Al molar ratio of about 2.5 to 2.7. Therefore, hydroxy-Al montmorillonite was prepared by reacting Na-mont-

morillonite with Al solutions at an OH/Al molar ratio of 2.5, in order to saturate the cation-exchange capacity of the clay. The interactions of citric acid with the hydroxy-interlayer montmorillonite at millimolar and submillimolar initial citrate concentrations and at low initial citrate/Al molar ratios then were characterized by adsorption measurements, chemical speciation techniques, and X-ray powder diffraction to delineate the accessibility and stability of the hydroxy interlayers in the presence of citric acid over a broad range of pH.

MATERIALS AND METHODS

Hydroxy-Al montmorillonite

Montmorillonite sample SWy-1 (Crook County, Wyoming) was obtained from the Source Clays Repository of The Clay Minerals Society. In the Na-saturated form, this clay mineral has the unit-cell formula (Weaver and Pollard, 1973):



corresponding to a theoretical cation-exchange capacity (CEC) of 85 meq/100 g.

Sixty grams of the crude montmorillonite were mixed in one liter of deionized water for 30 min with a mechanical stirrer. The fraction of equivalent-spherical-diameter particles $<0.5 \mu\text{m}$ was separated by centrifugation and then flocculated by adding 800 ml of a mixed solution of 1 M NaClO_4 and 0.001 M HClO_4 . The flocculated sample then was placed into six, 250-ml polyethylene centrifuge bottles and washed several times with the acidic NaClO_4 solution until the pH of the supernatant solution was 3. The sample was washed immediately thereafter with a 0.1 M NaClO_4 solution until the pH value rose to about 5.5, then washed a few times with deionized water to lower the sodium concentration. The solids content was determined gravimetrically, and the suspension was kept in a cold room at 5°C a few days before reaction with the Al polycations. X-ray powder diffraction (XRD) of the stock Na-montmorillonite showed that it contained a small amount of quartz impurity. Its CEC was determined by the ammonium acetate method to be 82 ± 2 meq/100 g, in good agreement with the calculated unit-cell value.

A solution of $\text{Al}(\text{OH})_{2.5}^{0.5+}$ polycations was prepared by adding dropwise 0.1 M NaOH to a fresh 0.2 M $\text{Al}(\text{ClO}_4)_3$ solution. The clay suspension and the fresh hydroxy-Al solution were mixed quickly, then aged 10 days at laboratory temperature ($24^\circ \pm 1^\circ\text{C}$). This sample ("Wy-AIOH") contained 11% $\text{Al}(\text{OH})_{2.5}$ by mass or, expressed in terms of $\text{Al}(\text{OH})_{2.5}^{0.5+}$ charge, about 90 meq/100 g of pure montmorillonite. Direct measurement of the CEC using the method of Gillman (1979) gave 31.0 ± 0.2 meq/100 g for this sample. A second hydroxy-Al montmorillonite sample, prepared in the same manner as sample Wy-AIOH, was found

to have a Gillman CEC of 20.2 ± 0.5 meq/100 g. This difference likely reflects the difficulty of preparing hydroxy-Al solutions and clays reproducibly (Bertsch, 1989).

Sorption experiments

A mixture of citric acid solution, NaClO_4 , and NaOH (or HClO_4) solutions was prepared in each of eight polypropylene centrifuge tubes. Aliquots of the Wy-AIOH stock suspension of known concentration were added then mixed quickly. The tubes were placed into a thermostatted water bath and shaken gently for 4 hr at 25°C . The solids content of the reacting mixture (C_s) and its initial citric acid concentration (C_i) were determined accurately by weighing the tubes at the different steps, taking into account the solids content of the stock suspension. All initial solutions were outgassed with N_2 before mixing to avoid excess carbonate concentrations. Organic-carbon-free deionized water and a carefully washed reaction vessel were used in all steps.

Preliminary experiments showed that mixing the suspension of hydroxy-Al montmorillonite and a solution of citric acid prepared at pH 5 led to a significant proton consumption during the first hour of reaction. The determination of sorbed citrate and dissolved Al (see below) for samples shaken between 2 and 30 hr showed that both increased slightly with time. This kinetic effect was probably not related to sorption phenomena, which generally are very fast (see, e.g., Zhang *et al.*, 1985). On the other hand, Al-citrate complex formation at low Al/citrate molar ratios has been reported to require a few hours for equilibration (Öhman and Sjöberg, 1983; Motekaitis and Martell, 1984). Inasmuch as observed significant shifts in pH (if not compensated) were observed only during the first hour of reaction, an arbitrary time of 4 hr was chosen for equilibration in the sorption studies.

After 4 hr of reaction, the tubes were placed in a rotor head at room temperature and centrifuged at 35,000 g for 20 min in a cold room. The supernatant solutions were pipeted into glass tubes that contained small magnetic bars, then capped. The clay plugs were washed quickly once, centrifuged, then put back into suspension to prepare deposits for XRD analysis. The pH of the supernatant solutions was always measured immediately in the glass tubes. Concentrated nitric acid then was added to the supernatant solutions, and carbon analyses were generally made the same day or, at most, the next day after one night in storage at 5°C . The samples then were analyzed for cations. From the citric acid equilibrium concentration (C_e), C_i , and C_s , the amount of sorbed citrate (Q_{ads}) was calculated. The range of C_s was 18–21 g/liter. The Na concentrations were in the range 0.20–0.25 M; thus, the ionic strength in the experiments was about 0.22 M.

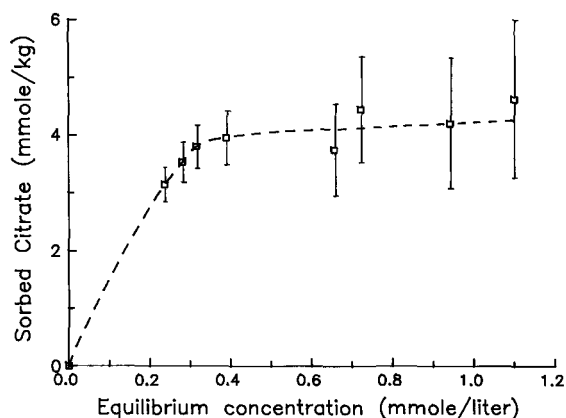


Figure 1. Sorption isotherm of citric acid on sample Wy-AIOH suspended in 0.02 M NaClO₄ at pH 5.3.

Analytical methods

Measurements of pH were made with an Orion Ross combination glass/calomel microelectrode filled with 0.1 M KCl or, for some solutions, with an Orion glass electrode and an Ag/KNO₃ reference electrode.

Citric acid concentrations were determined from total organic carbon (TOC) analysis with a Dohrmann-Xertex DC80 Carbon analyzer. The TOC values found for blanks (samples with only electrolyte solution and no citric acid at various pH values) were subtracted from sample values to determine C_e . The C_i values, obtained via TOC analyses, were in good agreement with those obtained via direct gravimetric determinations, assuming that the reagent dried 24 hr under vacuum over P₂O₅ had the anhydrous formula, C₆H₈O₇.

Al was determined by atomic absorption spectrometry (AAS) on a Perkin-Elmer model 5000 spectrophotometer using a nitrous oxide-acetylene flame. Mg and Na were determined by atomic absorption and by flame emission, respectively. These elements and others (particularly Si) were determined simultaneously by inductively coupled plasma-emission spectroscopy (ICP) for the solutions that contained little Al.

Quickly washed clay samples (either reacted with citric acid or blanks) were used to prepare oriented, air-dry deposits on glass slides for XRD analysis. They were examined between 2° and 42°2θ using a Siemens diffractometer equipped with a CuKα tube and a rear monochromator. The same deposits also were examined immediately after heating at 110°C overnight, and then again after having been heated at 300°C for 4 hr.

Chemical speciation of Al in the aqueous solutions was estimated using the program MICROQL-UCR (Coves and Sposito, 1986). The Davies equation (Sposito, 1981) was used to calculate the single-ion activity coefficients needed to compute conditional equilibrium constants from the thermodynamic equilibrium constants for citric acid dissociation and Al-citrate

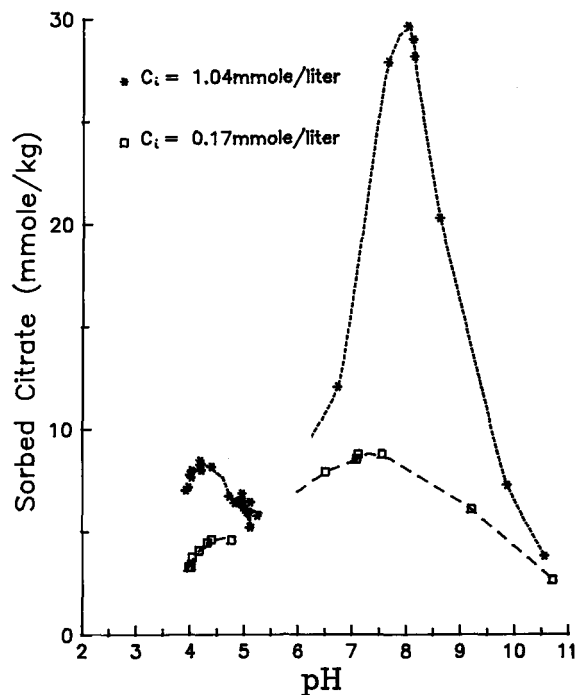


Figure 2. Sorption envelopes of citric acid on sample Wy-AIOH. * = $C_i = 1.04$ mmole/liter. □ = $C_i = 0.17$ mmole/liter.

complexes (Motekaitis and Martell, 1984; Gregor and Powell, 1986), Na-citrate complexes (Martell and Smith, 1977), and hydroxy-Al species (Nordstrom and May, 1989). These speciation calculations are valid so long as the total Al concentration (Al_T) refers exclusively to soluble Al, excluding metastable polymeric Al species. To test for this condition, results of Al_T determinations are presented below for supernatant solutions filtered with 0.025- μ m membranes. This filtration suppresses an important portion of polymeric Al ("Al_c," Bertsch, 1989), although the method is not yet completely satisfactory (Jardine *et al.*, 1986). No Al was extracted from the cellulose membrane filters by perchloric or citric acid, and the filters adsorbed no Al at pH 4 (data not shown).

RESULTS

Sorption data

Figure 1 shows a sorption isotherm measured at pH 5.36 ± 0.06 and $24^\circ \pm 1^\circ$ C for citrate on sample Wy-AIOH. The suspension density was 18.7 ± 0.9 g/kg solution. The data indicate a plateau near 4 mmole/kg for $C_e > 0.5$ mmole/liter, which is relatively low, compared with metal oxides (Bowden *et al.*, 1980; Zhang *et al.*, 1985), even taking into account that only 11% of the sample was expected to bind citrate. It is also low compared with a soil containing natural Al-hy-

Table 1. Chemical data relating to the lower adsorption envelope in Figure 2.

| pH _e | C _e (mmole/liter) | Al _T ¹ | log K _s ² | Al _{in} ³ (%) | Al _{org} ⁴ (%) | Free citrate ⁵ | |
|-----------------|---------------------------------|------------------------------|---------------------------------|--------------------------------------|---------------------------------------|---------------------------|-----|
| | | | | | | (mole/liter) | (%) |
| 3.96 | 0.104 | 6.89 | -32.86 | 98 | 1.5 | 1·10 ⁻⁸ | 0.0 |
| | | 6.74 | | | | 5·10 ⁻⁹ | |
| 4.01 | 0.102 | 5.48 | -32.81 | 98 | 1.9 | 1·10 ⁻⁸ | 0.0 |
| | | 5.48 | | | | 4·10 ⁻⁹ | |
| 4.04 | 0.094 | 4.22 | -32.83 | 98 | 2.2 | 1·10 ⁻⁸ | 0.0 |
| | | 4.41 | | | | 4·10 ⁻⁹ | |
| 4.17 | 0.089 | 2.11 | -32.77 | 96 | 4.2 | 1·10 ⁻⁸ | 0.0 |
| | | 2.07 | | | | 4·10 ⁻⁹ | |
| 4.31 | 0.082 | 0.97 | -32.72 | 92 | 8.5 | 2·10 ⁻⁸ | 0.0 |
| | | 0.96 | | | | 4·10 ⁻⁹ | |
| 4.40 | 0.078 | 0.60 | -32.70 | 87 | 13 | 2·10 ⁻⁸ | 0.0 |
| | | 0.58 | | | | 4·10 ⁻⁹ | |
| 4.76 | 0.079 | 0.163 | -32.48 | 52 | 48 | 4·10 ⁻⁸ | 0.1 |
| | | | | | | 3·10 ⁻⁹ | 0.0 |
| 4.76 | 0.079 | 0.136 | -32.65 | 42 | 58 | 6·10 ⁻⁸ | 0.1 |
| | | | | | | 5·10 ⁻⁹ | 0.0 |
| 6.50 | ~0.02 | 0.059 | -30.46 | 69 | 31 | 4·10 ⁻⁷ | 2.3 |
| | | | -30.48 | 66 | 34 | 1·10 ⁻⁹ | 0.0 |
| 6.50 | ~0.02 | 0.027 | -31.03 | 41 | 59 | 1·10 ⁻⁶ | 6.6 |
| | | | -31.23 | 26 | 74 | 6·10 ⁻⁹ | 0.0 |
| 7.08 | <0.01 | 0.013 | -31.44 | 84 | 16 | 5·10 ⁻⁶ | 53 |
| | | | -31.97 | 25 | 75 | 2·10 ⁻⁷ | 1.9 |
| 7.08 | <0.01 | <0.001 | -32.62 | 71 | 29 | 8·10 ⁻⁶ | 80 |
| | | | -34.56 | 0.8 | 99 | 8·10 ⁻⁶ | 76 |
| 7.10 | <0.01 | 0.029 | -31.08 | 90 | 10 | 4·10 ⁻⁶ | 42 |
| | | | -31.21 | 66 | 34 | 4·10 ⁻⁸ | 40 |
| 7.10 | <0.01 | <0.001 | -32.63 | 74 | 26 | 8·10 ⁻⁶ | 80 |
| | | | -34.52 | 0.9 | 99 | 8·10 ⁻⁶ | 76 |
| 7.55 | <0.01 | 0.011 | -31.89 | 98 | 2.1 | 8·10 ⁻⁶ | 80 |
| | | | -32.32 | 36 | 64 | 3·10 ⁻⁶ | 25 |
| 7.55 | <0.01 | <0.001 | -32.93 | 98 | 2.3 | 8·10 ⁻⁶ | 83 |
| | | | -33.72 | 16 | 84 | 8·10 ⁻⁶ | 76 |
| 9.20 | ~0.05 | 0.082 n.d. | -32.65 | 100 | 0.0 | 4·10 ⁻⁵ | 83 |
| 10.7 | ~0.10 | 1.90 | -32.80 | 100 | 0.0 | 8·10 ⁻⁵ | 83 |
| | | 1.76 | | | | | |

¹ Al_T = total Al concentration in the supernatant solution. If two values are given at the same pH, upper value determined before filtration through a 0.025- μ m membrane filter, lower value after filtration.

² K_s = (Al³⁺)(OH⁻)³ (ion activity product), calculated after speciation computations with the average Al_T if the two values were not significantly different. Differing results were obtained at 6 < pH < 9 with stability constants from Gregor and Powell (1986) vs. those from Motekaitis and Martell (1984), and are presented in this order.

³ Al_{in} = % Al_T as inorganic species.

⁴ Al_{or} = % Al_T as citrate complexes.

⁵ Free citrate = not bound to Al or Na. Different results were obtained at all pHs with constants from the two references cited in note 2 above.

droxy montmorillonite (Traina *et al.*, 1987). In keeping with this relatively weak sorption, the isotherm shape at low C_e is L-type (Sposito, 1984).

Figure 2 shows two sorption envelopes based on the initial concentrations: C_i = 0.170 \pm 0.003 or 1.04 \pm 0.02 mmole/liter. The corresponding values of C_e are listed in the second columns of Tables 1 and 2. The suspension density C_s was maintained at 20.2 \pm 0.4 g/liter. Below pH 6, the envelopes had the form typical of acids with low pK_a values (Hingston, 1981). At pH

>6, a second, larger maximum in sorption was observed at pH 7.5–8.0, instead of the usual decrease caused by an increasingly negative surface charge. For the lower sorption envelope (C_i = 0.17 mmole/liter), this maximum was controlled by the total amount of citric acid, because C_e < 0.01 mmole/liter.

Total Al concentrations in the supernatant solutions (Al_T) are listed in the third columns of Tables 1 and 2. At pH < 4.5, these concentrations and those of citric acid were not affected by recentrifugation or by filtra-

Table 2. Chemical data relating to the upper adsorption envelope in Figure 2.

| pH _e | C _e (mmole/liter) | Al _T ¹ | log K _s ² | Al _{in} ³ (%) | Al _{org} ⁴ (%) | Free citrate ⁵ | |
|-----------------|---------------------------------|------------------------------|---------------------------------|--------------------------------------|---------------------------------------|--|------------|
| | | | | | | (mole/liter) | (%) |
| 3.92 | 0.930 | 6.30 | -33.08 | 85 | 15 | 2·10 ⁻⁷ 7·10 ⁻⁸ | 0.0 |
| 3.99 | 0.913 | 5.56 | -32.93 | 84 | 16 | 1·10 ⁻⁷ 5·10 ⁻⁸ | 0.0 |
| 4.03 | 0.895 | 4.78 | -32.89 | 81 | 19 | 1·10 ⁻⁷ 5·10 ⁻⁸ | 0.0 |
| 4.03 | 0.906 | 3.89 | -33.01 | 77 | 23 | 2·10 ⁻⁷ 6·10 ⁻⁸ | 0.0 |
| 4.21 | 0.882 | 2.59 | -32.72 | 66 | 34 | 1·10 ⁻⁷ 4·10 ⁻⁸ | 0.0 |
| 4.19 | 0.881 | 2.63 | -32.77 | 66 | 34 | 2·10 ⁻⁷ 4·10 ⁻⁸ | 0.0 |
| 4.19 | 0.899 | 2.41 | -32.83 | 63 | 37 | 2·10 ⁻⁷ 5·10 ⁻⁸ | 0.0 |
| 4.40 | 0.898 | 2.07 | -32.34 | 57 | 43 | 1·10 ⁻⁷ 2·10 ⁻⁸ | 0.0 |
| 4.72 | 0.894 | 1.30 | -31.91 | 31 | 69 | 1·10 ⁻⁷ 1·10 ⁻⁸ | 0.0 |
| 4.82 | 0.903 | 1.33 | -31.61 | 32 | 68 | 9·10 ⁻⁸ 6·10 ⁻⁹ | 0.0 |
| 4.97 | 0.905 | 1.33 | -31.23 | 32 | 68 | 7·10 ⁻⁸ 3·10 ⁻⁹ | 0.0 |
| 5.05 | 0.912 | 1.33 | -31.05 | 32 | 68 | 6·10 ⁻⁸ 2·10 ⁻⁹ | 0.0 |
| 5.11 | 0.910 | 1.34 | -30.89 | 33 | 67 | 5·10 ⁻⁸ 2·10 ⁻⁹ | 0.0 |
| 6.73 | 0.829 | 1.11 | -29.45 -29.73 | 50 26 | 50 74 | 3·10 ⁻⁶ 2·10 ⁻⁸ | 0.4 0.0 |
| 7.65 | 0.486 | 0.48 | -30.58 -31.46 | 57 7.6 | 43 92 | 6·10 ⁻⁵ 3·10 ⁻⁵ | 13 7.1 |
| 8.01 | 0.399 | 0.32 | -31.06 -31.54 | 65 21 | 35 79 | 1·10 ⁻⁴ 1·10 ⁻⁴ | 36 31 |
| 8.11 | 0.463 | 0.25 | -31.31 -31.72 | 58 23 | 42 77 | 2·10 ⁻⁴ 2·10 ⁻⁴ | 46 49 |
| 8.13 | 0.431 | 0.38 | -31.06 -31.38 | 70 34 | 30 66 | 2·10 ⁻⁴ 2·10 ⁻⁴ | 40 35 |
| 8.60 | 0.645 | 0.18 | -31.81 -31.79 | 77 79 | 33 21 | 5·10 ⁻⁴ 5·10 ⁻⁴ | 72 78 |
| 9.86 | 0.923 | 0.48 | -32.54 | 100 | 0.2 0.0 | 8·10 ⁻⁴ 8·10 ⁻⁴ | 83 |
| 10.6 | 0.993 | 2.15 | -32.63 | 100 | 0.0 | 8·10 ⁻⁴ | 83 |

¹ Al_T = total Al concentration in the supernatant solutions.

² K_s = (Al³⁺)(OH⁻)³ (ion activity product). Different results were obtained at 6 < pH < 9 with stability constants from Gregor and Powell (1986) vs. those from Motekaitis and Martell (1984), and are presented in this order.

³ Al_{in} = % Al_T as inorganic Al species.

⁴ Al_{org} = % Al_T as citrate complexes.

⁵ Free citrate = not bound to Al or Na. Different results were obtained at all pHs with equilibrium constants from the two references cited in note 2 above.

tion through a 0.025- μ m membrane filter (Table 1). At pH < 4.1, Al_T was controlled principally by pH (cf. Tables 1 and 2 at comparable pH), whereas at 4.1 < pH < 4.5, C_e influenced Al_T (e.g., Al_T \approx 2 and 0.6 mmole/liter for C_e \approx 0.9 and 0.08 mmole/liter, respectively, at pH 4.4). At pH > 4.5, and particularly at pH > 6, filtration and recentrifugation both affected Al_T

significantly (Table 1), indicating the removal of particles containing Al (Jardine *et al.*, 1986). ICP analysis of the unfiltered supernatant solutions showed that the Si/Al and Mg/Al molar ratios were < 0.07 and < 0.03, respectively. Thus, at pH < 6, even if particles were present, the supernatant solution Al came from the montmorillonite interlayer (or possibly external) hy-

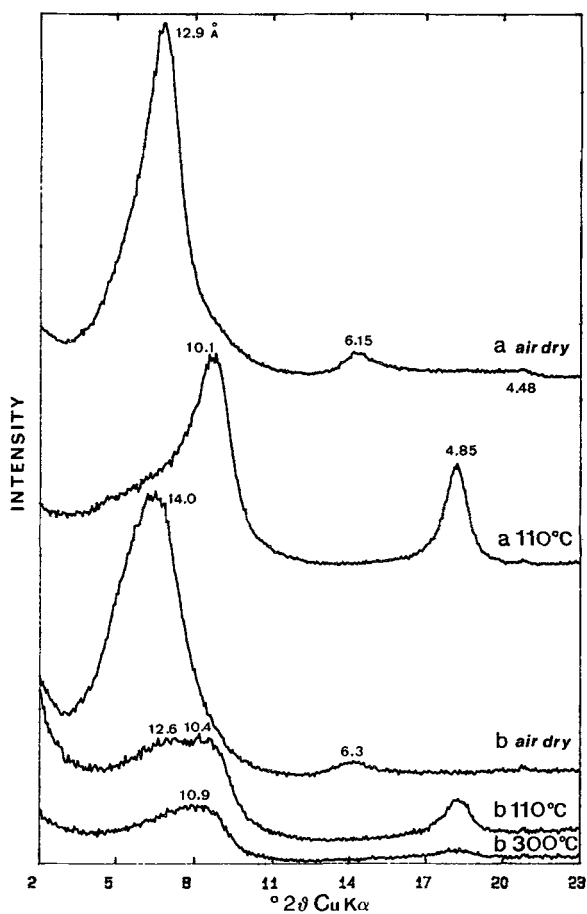


Figure 3. X-ray powder diffraction diagrams of oriented hydroxy-Al-montmorillonite deposits, before and after heating at 110° or 300°C. (a) Sample related to the upper curve of Figure 2, pH 6.7, $C_e \approx 0.8$ mmole/liter; (b) blank sample shaken 4 hr with NaOH (+ 0.02 M NaClO₄), final pH 7.9, no citrate.

droxy-Al material and not from the structure of the clay mineral. At higher pH, particularly $7 < \text{pH} < 9$, the sensitivity of the ICP and AAS analyses was not sufficient to permit this conclusion.

XRD data

Figure 3 shows XRD patterns of sample Wy-AIOH in the presence of citrate ($C_i = 1.04$ mmole/liter, $C_e \approx 0.08$ mole/liter) and in the absence of citrate at neutral or slightly alkaline pH. Samples that were reacted for 4 hr at these pHs in the presence of citric acid at the higher initial concentration showed essentially the behavior of Na-montmorillonite; i.e., a $d(001)$ value between 12.5 and 13 Å at laboratory relative humidity, which dropped to 10.0–10.2 Å immediately after heating at 110°C. This effect of heating was reversible. Some differences from the XRD pattern of Na-Wyoming montmorillonite (Brindley and Brown, 1981) were noted: slightly larger d -values and greater asymmetry of

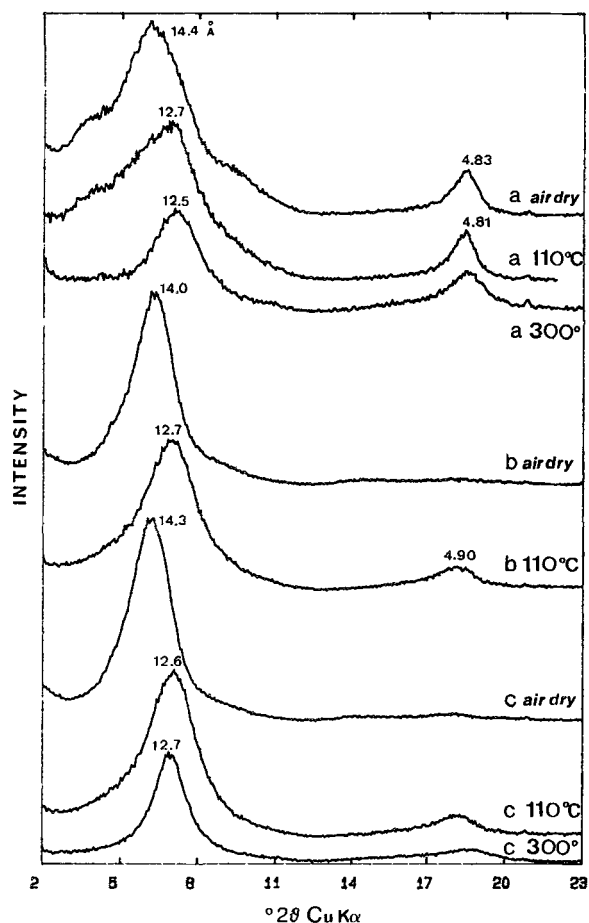


Figure 4. X-ray powder diffraction diagrams of oriented hydroxy-Al-montmorillonite deposits, before and after heating at 110° or 300°C. (a) Stock suspension sample; (b) blank sample shaken 4 hr with HClO₄ (+ 0.02 M NaClO₄), final pH 4.0, no citrate; (c) sample related to the upper curve of Figure 2, pH 4.0, $C_e \approx 0.9$ mmole/liter.

the peaks in the direction of smaller diffraction angles. Samples that had been shaken 4 hr at very high pH (e.g., pH 10.6) without citric acid also showed essentially the behavior of Na-montmorillonite. On the other hand, samples that were reacted at neutral or slightly alkaline pH without citric acid retained their Al-hydroxy interlayers, as seen from the absence of complete collapse to 10 Å after heating at 110° or 300°C (Figure 3b).

Samples reacted at pHs of about 5, or at lower pHs, either with or without citric acid (Figures 4b, 4c, and 5b) had XRD diagrams very similar to those of the two unreacted samples (Figures 4a and 5a). These two latter samples were different, as noted above, having d -values at 14.4 and 19 Å, respectively, at about 50% relative humidity. These results are consistent with those of a number of other investigators who have reported XRD patterns of Wyoming montmorillonite after reaction with Al-hydroxy solutions (Brydon and

Kodama, 1966; Webber and Clark, 1969; Lahav *et al.*, 1978; Brindley and Kao, 1980).

Samples reacted at a low initial concentration of citric acid and having a final pH of about 7 retained some interlayer material (Figure 5c). In fact, the XRD patterns indicated two peaks, at 14 and 10 Å, particularly after heating. In general, all samples reacted at a final pH > 7, even without citrate present (cf. Figures 3b and 4a), showed less stable interlayering and smaller d-values if heated.

DISCUSSION

In the range $4 < \text{pH} < 5.5$, given the low sorption of citric acid by hydroxy-Al montmorillonite and the absence of any effect of citric acid on the interlayer distance as determined by XRD, these organic molecules apparently did not react with the Al-hydroxy interlayer material. Kittrick (1983) noted pHs near 5 as the domain of metastability of hydroxy-Al clays. Therefore, hydroxy-polymers between the layers of the smectite, even those giving a $d(001)$ value of 19 Å under laboratory relative humidity, were not accessible to citric acid at millimolar concentrations within a 4-hr reaction time.

High pH, high citric acid concentration, and long reaction time, however, are factors that favor the transformation of hydroxy-Al smectite into a separate system, i.e., smectite-Al(OH)₃. Turner and Brydon (1967) and Hsu (1968) showed by solubility products, exchange properties, and XRD diagrams that high OH/Al ratio and aging lead to separate smectite and gibbsite phases after weeks or months. In the present experiments, a dramatic change occurred after a much shorter time in the presence of sufficient amounts of citric acid; the organic acid favored kinetically the transformation from hydroxy-Al smectite to (smectite + hydroxy-Al phase) at neutral pH. The Al-hydroxy polymers that left the interlayer region, however, could not have crystallized into gibbsite, but must have remained X-ray amorphous and co-precipitated with citrate (Huang and Violante, 1986). This association is illustrated by enhanced sorption at neutral and slightly alkaline pH (Figure 2).

The mechanisms that underlie these phenomena can be simply described: the Al polycations at pH 5 were bound to the clay both electrostatically and chemically, but at pH > 5 they were gradually neutralized, and their interaction with the clay decreased. Only then did citrate reach and become chemisorbed on aluminous surface sites. This sorption reaction decreased further, or even reversed the polymer interaction with the clay, which then dispersed like a Na-smectite.

Soluble Al may have competed with Al-hydroxide surfaces for citrate to form complexes. Thus, solution Al species must be examined to understand the adsorption data fully. The values of the logarithm of K_s

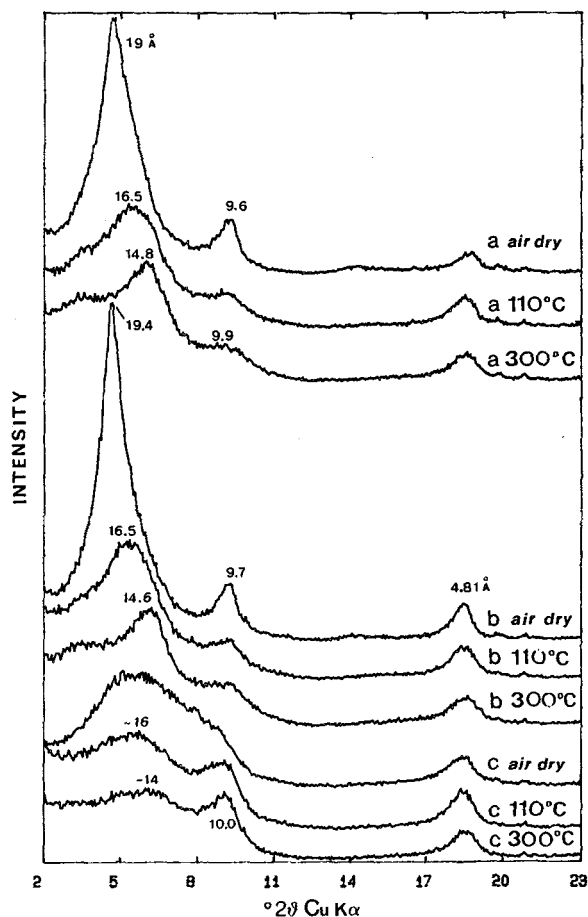


Figure 5. X-ray powder diffraction diagrams of oriented hydroxy-Al-montmorillonite deposits, before and after heating at 110° or 300°C. (a) Stock suspension sample; (b) sample related to the lower curve of Figure 2, pH 4.8, $C_c \approx 0.08$ mmole/liter; (c) sample related to the same curve, pH 7.1, $C_c < 0.01$ mmole/liter.

$\equiv (\text{Al}^{3+})(\text{OH}^-)^3$, calculated with free Al^{3+} concentrations estimated by the program MICROQL-UCR (Coves and Sposito, 1986) are listed in the fourth columns of Tables 1 and 2. The $\log K_s$ values were roughly constant in the ranges at pH < 4.4 and pH > 9 (including a $\log K_s$ value found after filtration at pH 4.76): $\log K_s = -32.7 \pm 0.2$. This result is in agreement with those from the extended studies of the $\text{Al}(\text{OH})_3$ solubility product by Turner and Brydon (1967), if only their hydroxy-Al clays aged less than one month are considered. For $5 < \text{pH} < 7$, however, polymeric Al was likely present in the supernatant solutions after one centrifugation; Al_T therefore is erroneously high, and the values of $\log K_s$ are correspondingly too large (see the data in Table 1, especially before filtration, and in Table 2).

These conclusions, of course, must be taken in the context of the "numerical" variability of Al speciation caused simply by the choice of Al-citrate complex sta-

bility constants. The present choice of those published by Gregor and Powell (1986) and Motekaitis and Martell (1984) was based on the fact that the first authors used potentiometric titration and ^{13}C NMR spectroscopy to argue for their species and against the species $(\text{Al}_3(\text{OH})_4(\text{Cit})_3)^{4-}$ proposed by Öhman and Sjöberg (1983). Motekaitis and Martell (1984) presented a simpler picture of Al-citrate complexes than did Gregor and Powell (1986), although the former used larger ranges for the ligand : metal ratio and pH in their experiments.

The speciation data in the last four columns of Tables 1 and 2 indicate that, at $\text{pH} > 6$, OH competed effectively with citrate for soluble Al, and the concentration of free citrate ion rose sharply. (At $\text{pH} < 4.4$, the Al-citrate concentration also dropped because of the competition between H^+ and Al^{3+} for citrate ions.) The overestimation of Al_7 near $\text{pH} 7$ could only have added to this trend of increasing free citrate concentration at $\text{pH} > 6$. Thus, the question is whether the increase in free citrate concentration overcompensated the decrease in citrate affinity for the surface and created the large second peak in the sorption envelopes near $\text{pH} 8$. The answer to this question is negative, as can be inferred from the XRD patterns, which show the decrease in affinity of the clay mineral for hydroxy-Al material in the interlayer region at alkaline pH, under conditions still favorable to a close association of citrate and Al within a solid phase.

SUMMARY AND CONCLUSIONS

Citrate sorption data, XRD patterns of the montmorillonite adsorbent, and chemical speciation of the aqueous solution phase are consistent with a simple mechanism for the citrate-hydroxy-Al-montmorillonite reaction at millimolar initial citric acid concentrations. At $\text{pH} < 5$, the interlayer hydroxy-Al material was stable and did not react significantly with citrate ions. Citrate adsorbed on the external hydroxy-Al polymers and yielded an adsorption envelope characteristic of an acid having a low pK_a . At $\text{pH} > 7$, the interlayer hydroxy-Al material quickly desorbed from the montmorillonite basal planes and formed with citrate an external, X-ray-amorphous solid. This reaction produced a large, second peak in the sorption envelope near $\text{pH} 8$, the shape of which was controlled by the surface charge and the amount of citrate available to react.

In the genesis of interlayer aluminum hydroxide, anions such as carboxylate (Goh and Huang, 1984) or phosphate (Kodama and Webber, 1975) may partly replace the hydroxyls and thus occur between the layers (Violante and Huang, 1985). Hydroxy-Al polycations, however, are bound strongly to montmorillonite at pH of about 5, and are inaccessible to citrate. The adsorption of anions by acid soils (e.g., Traina *et al.*, 1987) therefore should be attributed instead to external hy-

droxy-Al surfaces, not to the interlayer material. On the other hand, the presence of citrate ligands in the soil solution should facilitate considerably the destabilization of hydroxy-Al montmorillonite in response to increasing pH. Recall that the effect of liming on the retention of anions such as phosphate or borate is often not only related to the presence of Ca, but also to the chemistry of Al (Haynes, 1982). The present study suggests that reactive hydroxy-Al species can come rapidly out of the interlayer space, if the pH of an acid soil is increased, because of the presence of reactive organic ligands.

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