INFLUENCE OF CITRIC AND TANNIC ACIDS ON HYDROXY-Al INTERLAYERING IN MONTMORILLONITE

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Abstract—The formation of hydroxy-Al-interlayered montmorillonite was affected by complexing organic acids. Montmorillonite (<2.0 μm) was aged for three months at an initial pH of 5.0 or 6.0 in $AlCl_3$ solutions containing citric or tannic acid at organic acid/Al molar ratios from 0 to 1.0. The Al/clay ratio in the system was 900 meq Al^{3+}/100 g of montmorillonite. Ion-exchange experiments revealed that organically complexed Al ions have both positive and negative charges. Evidence from X-ray powder diffraction, electron microscopic examination, measurements of specific surface, cation-exchange capacity, organic carbon, and the nature of sorbed Al indicates that citric and tannic acids influence differently the hydroxy-Al interlayer formation in montmorillonite. Hydroxy-Al-citrate can be adsorbed as interlayers in montmorillonite, but hydroxy-Al-tannate exists principally as a separate phase binding the clay particles. The differences observed between the influence of citric and tannic acids on Al interlayering are probably due to their differences in molecular weight (size) and structure.

Key Words—Al polymers, Hydroxy-Al interlayer, Ion-exchange resin, Montmorillonite, Organic acid, Specific surface.

INTRODUCTION

Aluminum interlayering of expandable 2:1 clay minerals is a well-known natural process (Pearson and Ensminger, 1949; Sawhney, 1958; Dixon and Jackson, 1960; Rich, 1968) and has been successfully reproduced in laboratory studies (Shen and Rich, 1962; Turner and Brydon, 1965; Violante and Violante, 1978). The formation of Al-interlayered clay is accompanied by changes in many properties of the original clay minerals, such as a reduction in the cation-exchange capacity (CEC) (Jackson, 1963; Rich, 1968; Hsu, 1968), the development of pH-dependent layer charge (de Villiers and Jackson, 1967), the appearance of a titratable third-buffer-range acidity (Schwertmann and Jackson, 1963), stable 14-Å X-ray powder diffraction spacings, modification to the retention and movement of certain anions, and changes in the physical and engineering properties of the clays (Barnhisel, 1977). The formation of Al interlayers in montmorillonite occurs readily in moderately acid conditions and is affected by the presence of inorganic cations and anions in the systems (Rich, 1968; Turner and Brydon, 1967; Hsu, 1968). Organic acids are part of natural environments (Förstner, 1981; Stevenson, 1982); they are introduced to the terrestrial and aquatic systems through natural vegetation and/or farming, and range from simple to complex molecules.

Kwong and Huang (1981) demonstrated that differences in the properties of the hydrolytic products of Al formed in the presence of low-molecular-weight organic acids (e.g., citric acid) and high-molecular-weight polyphenolic organic acids (e.g., tannic acid) are attributable to the differences in the chemical as well as the physical behavior of the organic acids. Goh and Huang (1984) reported that the citric acid/Al molar ratio significantly influenced the degree to which citric acid perturbed the formation of hydroxy-Al-montmorillonite complexes at the Al/clay ratio of 600 meq Al^{3+}/100 g. They further noted that a citrate/Al molar ratio of 0.5 was apparently critical in perturbing the formation of the hydroxy-Al-montmorillonite complexes. The differences in the mechanism by which citric and tannic acids would influence the formation of hydroxy-Al-montmorillonite was, however, not discussed. A study of the reactions of citric and tannic acids with hydroxy-Al and montmorillonite would therefore facilitate our understanding of the complex reactions of hydroxy-Al with montmorillonite in the presence of small and large chelating organic ligands.

The objective of the present study was to compare the influence of citric and tannic acids on the formation of hydroxy-Al-montmorillonite complexes in the pH range 5.00 and 6.00 which is most conducive to Al interlayering.

MATERIALS AND METHODS

Retention of Al-organic acid complexes by exchange resins

The resins used were Rexyn 101, H^+-exchange resin (CEC = 460 meq/100 g, 16–50 mesh average spherical diameter), Dowex 50W-X8, Na^+-exchange resin (CEC = 510 meq/100 g, 20–40 mesh average spherical diameter), and Dowex 1-X8, Cl^--exchange resin (anion exchange capacity = 420 meq/100 g, 20–50 mesh average spherical diameter). The two cation-exchange resins were chosen to test whether or not the dif-

ference in ionic forms, H^+ vs. Na^+, significantly affected the exchange properties of the Al-organic acid complexes.

The Al-organic acid complexes were prepared by pipeting 20 ml of 2.308×10^{-2} M $AlCl_3$ solution into 80 ml of deionized distilled water to which citric or tannic acid had been added so as to give organic acid/Al molar ratios of 0, 0.1, 0.5, and 1.0. The solutions which contained the Al-organic acid complexes were stirred for 20 min and the pH was recorded. The solution was then added dropwise to buret columns packed with 20 g of the appropriate exchange resin. The columns were 34 cm in length and 1 cm in diameter. The rate of addition and of elutriation was 2 ml/min. The elutriate was collected in a beaker and then passed through the column four more times to ensure that the exchange reaction was complete. At the end of the elutriation, the elutriate was analyzed for Al by the Aluminon method (Hsu, 1963) after destruction of organic acids by digestion with nitric and sulfuric acids (Weaver *et al.*, 1968). The percentage of Al exchanged was calculated by the difference between the concentration of Al in the initial Al-organic acid complexes in solution and the final concentration of Al in the elutriate.

Preparation and aging of mineral suspensions

Three liters each of 5×10^{-3} M $AlCl_3$ containing citric or tannic acid at the required organic acid/Al molar ratios of 0, 0.1, 0.3, 0.5, 0.7, and 1.0 were prepared using reagent grade chemicals. Five grams of montmorillonite (from Upton, Wyoming, previously saturated with Na by treating it with 1 M NaCl and then washing it free of Cl^-) were added from a 2% stock suspension to the solutions containing $AlCl_3$ and citric or tannic acid. The control treatment (sample F1) contained clay in water. The suspensions were then brought to a final volume of 4 liters or were titrated against 0.2 M NaOH (1 ml/min) before bringing to the final volume with deionized distilled water. The amount of 0.2 M NaOH added was such that the initial pH of the suspensions after dilution to the final volume was 5.00 or 6.00. The Al concentration in the solution after dilution was 3.75×10^{-3} M. The suspensions were aged at $25° \pm 0.5°C$ for 3 months in polypropylene bottles and were agitated daily. The initial and final pH of the suspensions were recorded. After 3 months of aging, each suspension was separated into its filtrate and solid phase by ultrafiltration through a Millipore MF filter of 0.025-μm pore size. The solid phase of each sample was then dialyzed in a SpectraPor 2 dialysis membrane tube (molecular weight cutoff = 12,000–14,000) against deionized distilled water, with constant renewal of water, for 72 hr until a negative test for Cl^- was obtained.

Examination of filtrate and solid-phase products

The total Al in the filtrate was determined by the Aluminon method (Hsu, 1963) after the organic acids were destroyed by digestion with nitric and sulfuric acids (Weaver *et al.*, 1968).

The surface reactivities of the solid-phase reaction products were analyzed with respect to their CEC, extractable Al, exchangeable Al, and specific surface. The CEC was determined according to the procedure outlined by Alexiades and Jackson (1965). Exchangeable Al was determined by washing 100 mg of the sample five times with 1 M KCl (10 ml each) and determining Al in the combined supernatant after centrifuging for 7 min at 1200 *g* each time. Acid-extractable Al was similarly determined in separate samples by five washings each of 7 min with 10 ml of 0.2 M HCl (Shen and Rich, 1962). The percentage of the adsorbed Al that was exchanged by 1 M KCl was calculated as follows:

% KCl-exchangeable Al

$$= \frac{\text{Amount of KCl-exchangeable Al}}{\text{Total Al removed from solution}} \times 100$$

The percentage of the fixed Al that was extracted by 0.2 M HCl was estimated as follows:

% fixed Al extracted by HCl

$$= \frac{\text{Fixed Al extractable by HCl}}{\text{Total fixed-Al}} \times 100$$

$$= \frac{(\text{Al extracted by HCl}) - (\text{KCl-exchangeable Al})}{(\text{Total Al sorbed}) - (\text{KCl-exchangeable Al})} \times 100$$

The carbon content of selected freeze-dried samples was determined by ignition and gas chromatography using a Hewlett Packard Carbon, Hydrogen, Nitrogen Analyzer.

The specific surface of the solid phase products was evaluated gravimetrically by the retention of ethylene glycol monoethylether (EGME) as proposed by Carter *et al.* (1965) and modified by Eltantawy and Arnold (1973) using a theoretical value of 3.71×10^{-4} g of EGME for a complete monomolecular layer coverage of 1 m^2 of surface. X-ray powder diffraction (XRD) analysis of oriented specimens was undertaken using Ni-filtered $CuK\alpha$ radiation. For infrared (IR) analysis, the KBr pellet method (1.5% w/w) was used on a Perkin Elmer 621 IR instrument. Dilute (0.1%) suspensions in deionized distilled water of selected samples were deposited on carbon-coated Formvar film on copper grids and dried at 35°C before examination with a Philips 400 transmission electron microscope.

RESULTS AND DISCUSSION

Retention of aluminum-organic acid complex by exchange resins

The results of the retention of Al by the cation and anion exchange resins are presented in Table 1. The fact that all the Al was retained by H^+- and Na^+-exchange resins demonstrates that the Al or Al-organic acid complex in solution possessed positively charged sites. The pH of the solution also indicates that the hydrolysis and polymerization of Al was insignificant (Kwong and Huang, 1979). At the same time, the complexes must also have possessed negatively charged sites. In the absence of organic acid, the pH of the solution (Table 1) was 3.90, and no Al was retained by the Cl^-–exchange resin. The addition of organic acid to the Al solution at citrate/Al ratios of 0.1, 0.5, and 1.0 successively increased the total Al retained by Cl^-–exchange resin to 8.2%, 13.3%, and 17.0%, respectively. The complexation reaction between citric acid and Al produces 1:1 and also 2:1 complexes (Kwong and Huang, 1979) which can further dissociate protons (Pattnaik and Pani, 1961). The negative logarithm of the first dissociation constant of the Al-citrate (pK) is 3.49 (Pattnaik and Pani, 1961). The negatively charged sites therefore must have arisen from the dissociation of protons from the Al-citrate complexes.

The dissociation constant of Al-tannic acid complexes has not been reported in the literature. Some Al, however, was also retained by the Cl^-–exchange

Table 1. Retention of Al-organic acid complexes by cation and anion exchange resins.

Organic acid	Organic acid/Al molar ratio	Solution pH	% Al exchanged		
			H+-resin	Na+-resin	Cl−-resin
Citric	0	3.90	100	100	0
	0.1	3.06	100	100	8.2 ± 1.9
	0.5	2.65	100	100	13.3 ± 1.6
	1.0	2.49	100	100	17.0 ± 2.1
Tannic	0.1	3.09	100	100	0
	0.5	2.87	100	100	0
	1.0	2.78	100	100	2.6 ± 0.02

resin at a tannate/Al ratio of 1.0, although to a lesser degree than that observed for Al-citric acid complexes (Table 1). According to Hsu and Rich (1960), the porosity of the resins determines the size of molecules that will diffuse into the resin. The retention of Al-citric acid complexes by the Cl−-exchange resin may have been easier than the retention of Al-tannic acid complexes because the latter has a larger size and may not have diffused to the exchange sites as easily.

pH

When citric acid was present in the system, smaller pHs were recorded up to a citrate/Al ratio of 0.5; above a citrate/Al ratio of 0.5, the pH of the systems actually increased from the initial values after 3 months of aging (Table 2). The smaller decreases in pH as the citrate/Al ratio was increased to 0.5, as compared to the pH drop in the controls (samples F3 and F9), were probably due to the buffering action of the citrate anion and the constraint that the anion had on the hydrolysis of Al (Kwong and Huang, 1977). At the citrate/Al ratios of 0.7 (sample F7) and 1.0 (samples F8 and F14), the increases in pH after 3 months of aging were probably due to partial breakdown of the hydroxy-Al polymers into smaller units under the influence of high citrate/Al molar ratios.

The final pHs of the systems aged with tannic acid (Table 2) indicate that more protons were produced by the hydrolysis of Al and by the complexation reaction between Al and tannic acid than could be buffered by the carboxylate groups on tannic acid. The pH decrease was partially due to the complexation between Al and the phenolic groups (McHardy et al., 1974). The larger number of functional groups per mole of tannic acid

Table 2. Surface properties of the solid phase reaction products of montmorillonite with hydroxy-Al ions and organic acids.

Sample[1]	Organic acid/Al molar ratio	pH		Al removed[2] from solution (mg/g)	Retained Al[3] exchanged by 1 M KCl (%)	Fixed Al[4] extracted by 0.2 M HCl (%)	Specific surface (m²/g)	CEC[5] before extraction by 0.2 M HCl (meq/100 g)	CEC after extraction by 0.2 M HCl (meq/100 g)
		Initial	Final						
F1	in water	7.35	7.37	0	0	>100	794	96	94
F2	in AlCl₃	3.80	3.70	5.94	44.9	>100	811	82	79
F3	0	5.00	4.45	79.89	4.8	15.3	322	17	34
F4	0.1	5.00	4.83	70.80	4.6	10.4	346	18	23
F5	0.3	5.00	4.85	41.91	14.1	29.6	498	34	51
F6	0.5	5.00	4.98	19.69	42.6	94.3	771	56	63
F7	0.7	5.00	5.25	2.71	100	>100	779	80	79
F8	1.0	5.00	5.54	0.79	100	>100	777	85	86
F9	0	6.00	4.93	80.95	4.9	13.2	326	18	42
F10	0.1	6.00	5.26	69.55	5.0	10.1	348	20	29
F11	0.3	6.00	5.49	43.69	10.5	18.9	490	37	43
F12	0.5	6.00	5.72	21.55	39.3	43.2	692	51	63
F13	0.7	6.00	6.00	4.99	60.1	78.9	780	79	67
F14	1.0	6.00	6.24	1.02	98.0	>100	771	83	94
F15	0.1	5.00	4.78	80.95	1.2	66.6	733	60	87
F16	0.3	5.00	4.89	80.95	4.6	46.6	785	94	34
F17	0.5	5.00	4.75	80.95	4.8	37.1	998	92	30
F18	0.7	5.00	4.87	73.23	4.5	33.9	1286	94	39
F19	1.0	5.00	4.76	66.72	4.4	21.2	1144	86	33
F20	0.1	6.00	5.72	80.95	0.8	57.7	733	54	71
F21	0.3	6.00	5.57	80.95	0.2	48.5	944	99	38
F22	0.5	6.00	4.93	80.95	3.7	37.8	1000	99	36
F23	0.7	6.00	4.65	80.95	6.2	35.3	1269	90	40
F24	1.0	6.00	4.62	75.06	4.6	29.4	1180	74	42

[1] Samples F4–F8 and F10–F14 were aged in presence of citric acid. Samples F15 to F24 were aged in presence of tannic acid. Samples F3 and F9 were aged in presence of hydroxy-Al ions without organic acids.
[2] Mean error of duplicates = ±0.43 mg Al/g clay.
[3] The average error is 4.7% of the values indicated.
[4] The average error is 3.5% of the values indicated.
[5] Mean error of duplicates = ±3 meq/100 g.

in comparison to citric acid also accounts for more proton generating sites in the former.

Exchangeability and extractability of Al removed from solution

The removal of Al from solution was influenced by the type of organic acid, the organic acid/Al molar ratio that was initially present in solution, and the pH of the medium (Table 2). In the absence of organic acid and NaOH (sample F2), only 5.94 mg of Al^{3+} was adsorbed per gram of montmorillonite. The aging of this sample at an initial pH of 3.80 for three months could also have caused some dissolution of the clay inasmuch as more than 100% of the fixed Al was removed by the five combined washes with 0.2 M HCl (Table 2). The small amount (0.79 mg/g) of Al extracted from the clay that was aged in water by the 0.2 M HCl was likely due to the dissolution of structural Al from montmorillonite. Increasing the citrate/Al ratio reduced the amount of Al that was removed from solution, because the citrate competed with the montmorillonite and formed soluble complexes with Al.

The perturbation of polymerization reactions of Al by citrate is shown in Table 2 by the results of the KCl-exchangeable Al (samples F4–F8 and F10–F14). According to Hsu (1968), stable hydroxy-Al polymers in montmorillonite have an OH/Al ratio of 2.5–2.7. In suppressing the hydrolysis of the Al^{3+}, the citrate ligands reduced the growth of the hydroxy-Al polymers and, hence, their net positive charge. Furthermore, the structural distortion in the interlayer sheet (see Goh and Huang, 1984) reduced the tenacity with which the hydroxy-Al-citrate polymers were held. Thus, the proportion of the adsorbed Al that was exchanged by 1 M KCl increased as the citrate/Al ratio increased to 1.0.

At both initial pHs of 5.00 and 6.00, a smaller proportion of Al was extracted by 0.2 M HCl at a citrate/Al ratio of 0.1 (samples F4 and F10, Table 2) as compared to samples where citric acid was absent (samples F3 and F9). Aluminum was increasingly more extractable, however, when the citrate/Al ratio was gradually increased, as was found by Goh and Huang (1984).

Increasing the tannate/Al ratio did not always reduce the amount of Al removed from solution (Table 2). The removal of Al from solution was probably due to adsorption by the clay and to precipitation as discrete oxides. The complexation reaction between Al and tannic acid generated protons, as shown below:

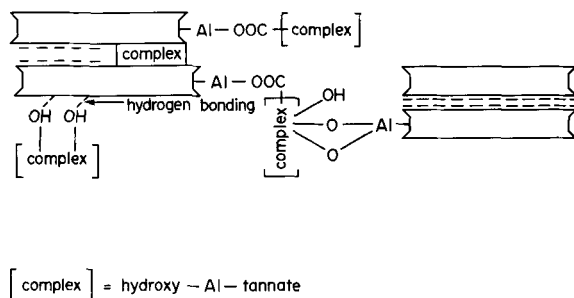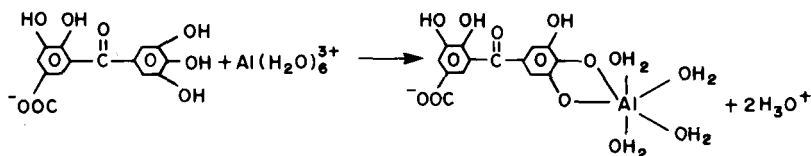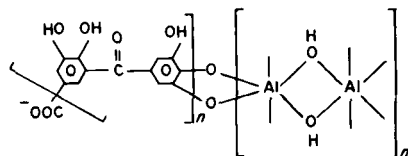[complex] = hydroxy – Al – tannate

Figure 1. Possible modes of interaction between hydroxy-Al-tannate complexes and external and internal surfaces of montmorillonite.

Further growth of the polymer was possible, and a large hydroxy Al-tannate complex formed, as illustrated below:

The high molecular weight of tannic acid caused the hydroxy-Al-tannate complexes to precipitate as a separate phase where they bridged adjacent clay particles through adsorption by montmorillonite and thus promoted the aggregation of clay particles as schematically represented in Figure 1.

The data show that hydroxy-Al-tannic acid-montmorillonite complexes had a much lower percentage of KCl-exchangeable Al than hydroxy-Al-citric acid-montmorillonite complexes at comparable organic acid/Al molar ratios (Table 2). This lower percentage of KCl-exchangeable Al indicates that most of the Al in the tannic acid systems was incorporated in the network of the hydroxy-Al-tannate complexes as a separate solid phase, albeit strongly bound to montmorillonite. Moreover, the percentage of Al that was extractable by the HCl solution in the tannic acid system decreased with increasing tannate/Al ratio, whereas the percentage of HCl-extractable Al in citric acid systems increased as the citrate/Al ratio increased from 0.1 to 0.7 (Table 2). This difference in extractability of Al by the HCl solution between tannic acid and citric acid systems is probably due to the differences in physical behavior between the two acids. Whereas citric
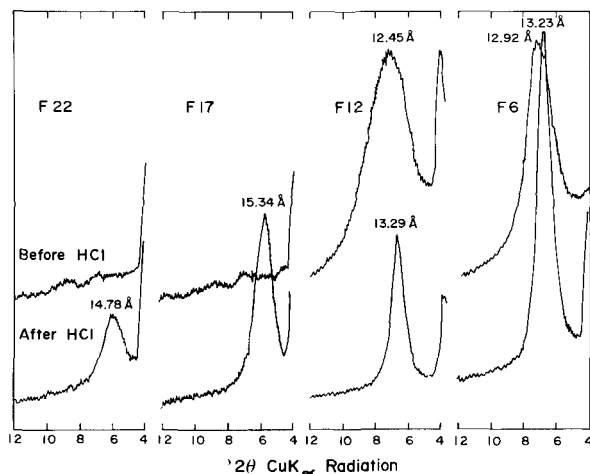
Figure 2. X-ray powder diffraction tracings of selected hydroxy-Al-organic acid-montmorillonite complexes before and after the 0.2 M HCl treatment. Sample numbers are explained in Table 2.

acid is a low-molecular-weight organic acid and is only weakly adsorbed by montmorillonite, tannic acid (M.W. = 1701) is strongly retained by physical forces because each point of contact is additive (Greenland, 1965; Kwong and Huang, 1981). The additive forces eventually led to aggregation of the montmorillonite particles by hydroxy Al-tannate complexes.

XRD, TEM, and IR observations

The perturbation of hydroxy-Al interlayering of montmorillonite caused by the two organic acids was further revealed by the XRD tracings in Figure 2. Broad 001 peaks of the samples aged in citric acid before HCl treatment were observed (samples F6 and F12). The aggregation of clay particles by the hydroxy-Al tannate complexes, however, resulted in an absence of definitive 001 peaks (samples F17 and F22, Figure 2) before the HCl treatment. The "cleansing" action of the HCl in removing hydroxy-Al-organic acid complexes responsible for the poor orientation of the clay is obvious from the XRD tracings before and after HCl treatment.

As mentioned above, the fundamental difference between the influence of hydroxy-Al-citrate and hydroxy-Al-tannate in causing structural disorientation of the montmorillonite particles is attributable to the vast difference in the molecular weight of the two organic acids. Thus, citric acid complexed with hydroxy-Al ions, and the hydroxy-Al-organic complexes were adsorbed in the interlamellar spaces of montmorillonite, increasing the structural distortion from within the internal surfaces (Goh and Huang, 1984). X-ray scattering and the random arrangement of montmorillonite particles (Figure 1) caused by the separate-phase hydroxy-Al-tannate complexes likely gave rise to the poor XRD patterns (Figure 2) of the samples aged in tannic acid. The following evidence from TEM and IR supports this interpretation. The absence of dark, noncrystalline phases and the highly dispersed nature of the clay platelets in the sample aged in citric acid (Figure 3a) is obvious. On the contrary, a discrete coating which binds the clay platelets in the samples aged in tannic acid is clearly present (Figure 3b).

The IR spectra of selected samples are presented in Figure 4. The stretching modes of Al–OH and H–OH
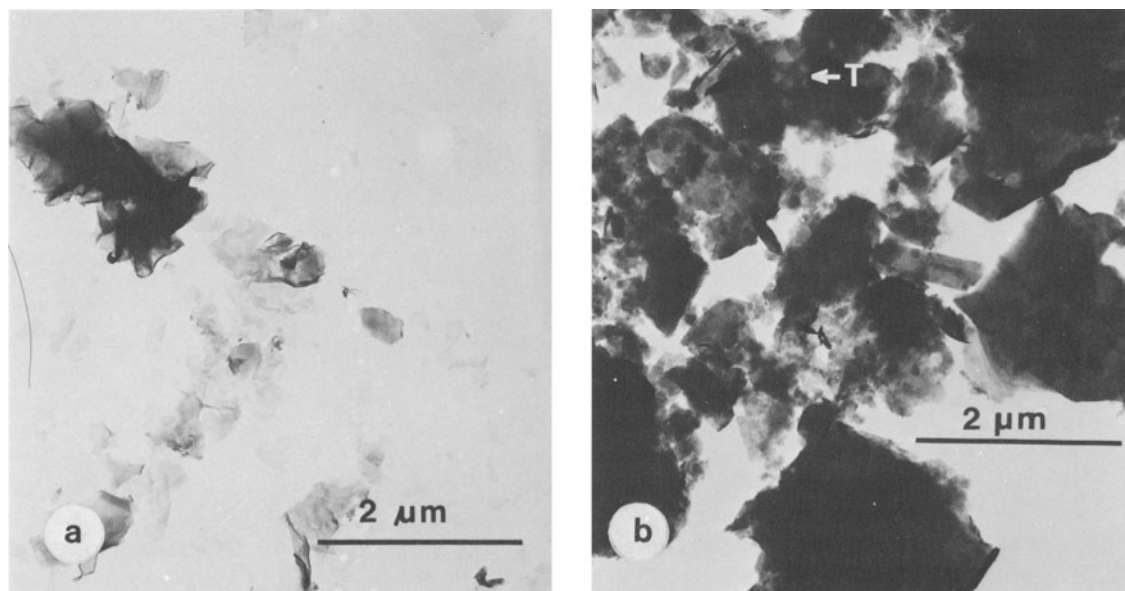

Figure 3. Transmission electron micrographs of hydroxy-Al-montmorillonite aged 3 months: (a) at citrate/Al molar ratio of 0.5 and initial pH of 6.0, and (b) at initial tannate/Al molar ratio of 0.5 and initial pH of 5.0; T = hydroxy-Al-tannate.

of montmorillonite produce absorption bands at 3640 and 3480 cm^{-1}, respectively (White, 1971; Van der Marel and Beutelspacher, 1976). The additional absorption bands at 3695 and 3570 cm^{-1} (Figures 4a and 4b) are the stretching modes of interlayer hydroxy-Al polymers (Weismiller *et al.,* 1967). For sample F9 (Figure 4b), which had been aged at the initial pH of 6 in the absence of citric acid, the absorption band at 3530 cm^{-1} is due to gibbsite (Hsu, 1977) which was not present at the initial pH of 5 (Figure 4a). The perturbation of hydroxy-Al interlayering by citric acid at a citrate/Al molar ratio of 0.5 resulted in the disappearance or reduction of the intensity of the two bands at 3695 and 3570 cm^{-1} (Figure 4c). No absorption bands were present which indicated discrete-phase hydroxy-Al-citrate (in the 1200–1600-cm^{-1} region, not shown) or Al hydroxides (3500–3600-cm^{-1} region). The absorption spectra of the sample aged in tannic acid (Figure 4d) were quite different from those of Figures 4a–4c. The absorption bands in the 3200–3700-cm^{-1} region were broad and are probably due to the COOH groups of separate-phase hydroxy-Al-tannate. In the 1200–1725-cm^{-1} region, sharp absorption bands corresponding to the functional groups and structure of gallotannic acid were observed.

Specific surface and cation-exchange capacity

The specific surface of the Na-saturated montmorillonite was about 800 m^2/g (Table 2) which is in agreement with the values reported by Jackson (1979) and Eltantawy and Arnold (1973). The specific surface of the montmorillonite decreased to about 320 m^2/g when hydroxy-Al interlayers were present (samples F3 and F9). As less Al was adsorbed at higher citrate/Al ratios, the original specific surface was regained. At the same time, charge blocking by fixed Al was also reduced such that the CEC of the samples increased as the citrate/Al ratio increased. The extraction of fixed Al (samples F3–F14) by 0.2 M HCl increased the CEC of the samples.

The specific surface of the solid phase in the tannic acid systems also increased at higher tannate/Al ratios, and in some products exceeded that of montmorillonite. The increase of specific surface beyond that of montmorillonite was likely due to molecular association between tannic acid and EGME.

Furthermore, tannic acid may have formed as separate-phase hydroxy-Al-tannate complexes. Thus, even though the amount of Al lost from solution was quite substantial (Table 2), the reduction in CEC was not significant except where the tannate/Al ratio was 0.1 or 1.0 (samples F15, F20, F19, and F24, Table 2). These results can be explained by the fact that at a tannate/Al ratio of 0.1, insufficient tannic acid was present to influence greatly the formation of hydroxy-Al interlayers in montmorillonite, and the CEC thus
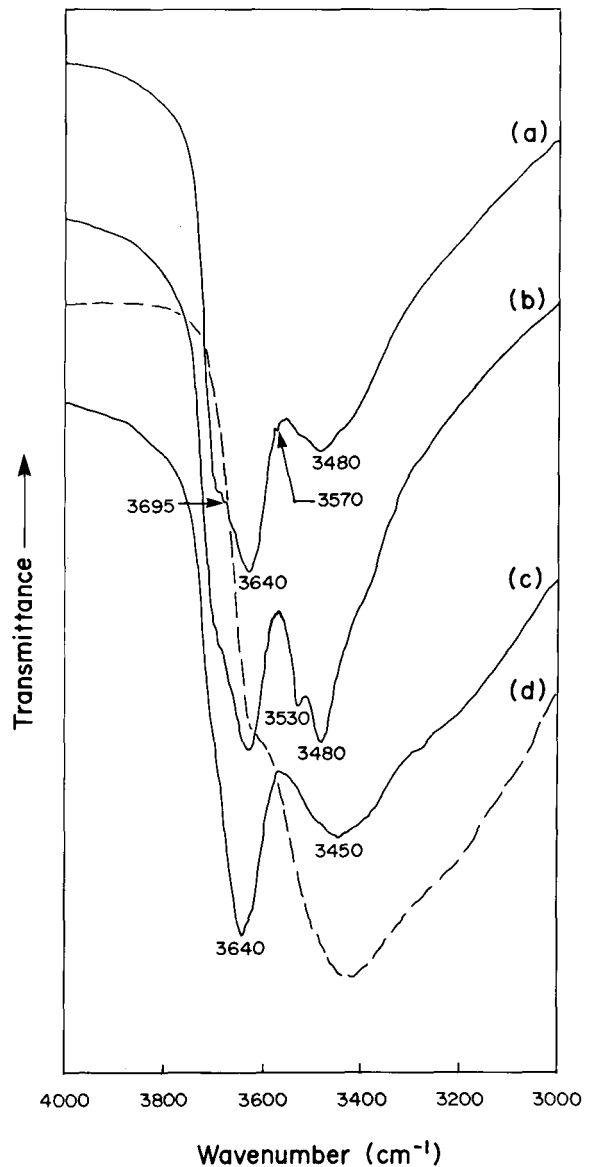

Figure 4. Infrared absorption spectra of selected hydroxy-Al-montmorillonite after 3 month aging: (a) at initial pH 5.0 in absence of organic acid; (b) at initial pH 6.0 in absence of organic acid; (c) at initial pH 5.0 and citric acid/Al molar ratio of 0.5; and (d) at initial pH 5.0 and tannic acid/Al molar ratio of 0.5.

decreased. Moreover, at a tannate/Al ratio of 0.1, the contribution to CEC from the small amount of tannate present was probably not substantial. At tannate/Al ratios between 0.3 and 0.7, the negative sites of dissociated tannic acid molecules increased the CEC. At a tannate/Al molar ratio of 1.0, less tannic acid was actually adsorbed (see following discussion on organic carbon); thus, its contribution to the CEC was not as high as was expected. Furthermore, the change in the

Table 3. Organic carbon content of selected solid-phase reaction products of montmorillonite with hydroxy-Al ions and organic acids.

Sample[1]	Organic acid/ Al molar ratio	After aging 3 months (%[2])	After 0.2 M HCl extraction (%[2])
F4	0.1	0.36	0.00
F6	0.5	0.53	0.27
F8	1.0	0.63	0.10
F15	0.1	14.97	1.76
F17	0.5	26.23	1.77
F19	1.0	14.08	2.04

[1] Samples F4–F8 were aged at initial pH of 5.00 in the presence of $AlCl_3$ and citric acid. Samples F15–F19 were aged at initial pH of 5.00 in the presence of $AlCl_3$ and tannic acid.
[2] Average precision = ±0.05%.

CEC of the solid phase after pretreatment with 0.2 M HCl (Table 2) shows that the CEC of samples F15 and F20 (tannate/Al ratio of 0.1) increased after the extraction of Al by the HCl solution. This increase is likely due to dissolution of the hydroxy-Al interlayers by the HCl solution. The dissolution of hydroxy-Al-tannate complexes in the samples aged at a tannate/Al ratio of 0.3 or higher caused a reduction in the CEC after pretreatment of the samples with 0.2 M HCl.

Organic carbon

Table 3 shows the organic carbon content of selected samples after they were aged for 3 months at the initial pH of 5.0 and after they were pretreated with 0.2 M HCl. The organic carbon content increased with increased citric acid/Al molar ratio after aging. It is noteworthy that sample F6 retained more organic carbon than sample F8 after the 0.2 M HCl treatment. Sample F6 retained about 6% of its fixed Al, whereas sample F8 contained no fixed Al following the same acid treatment (Table 2). Therefore, some of the organic carbon in sample F6 must have been fixed in the interlamellar spaces as hydroxy-Al-citrate complexes because the TEM and IR data did not reveal separate, discrete phases.

The organic carbon content of the hydroxy-Al-tannic acid-montmorillonite complexes (Table 3) increased as the tannate/Al ratio increased from 0.1 to 0.5. This increase was followed by a decrease in carbon content as the tannate/Al ratio increased to 1.0. This trend agrees with the amount of Al sorbed by the samples (Table 2) and was apparently due to the solubilization of hydroxy-Al-tannate complexes when the tannate/Al ratio was 1.0. Table 3 further shows that the carbon content of the montmorillonite complexes after the 0.2 M HCl extraction was higher at higher tannate/Al ratios and was probably due to the lower extractability of Al by the HCl solution in the samples as the tannate/Al ratio increased (cf. Table 2).

CONCLUSION

The retention of Al-organic acid complexes by cation- and anion-exchange resins indicate that positively and negatively charged sites are present in hydroxy-Al-organic acid complexes. The number of negative sites and hence the net negative charge of the Al-organic acid complexes increased as the organic acid/Al molar ratio increased.

The net positive charge of the hydroxy-Al-citrate polymer was reduced by the inclusion of citrate ligands into its network because the polymers were restricted in their growth and because of the contribution of negative charges from citrate. The data indicate that some of the hydroxy-Al-citrate complexes were adsorbed in the interlamellar spaces of montmorillonite. Because citric acid is a strong chelator of Al, the formation of soluble hydroxy-Al-citrate was, however, a competitive reaction to adsorption. Therefore, at citrate/Al molar ratios greater than 0.5, the solubilization effect was apparently far greater than the adsorption by montmorillonite.

The specific surface and CEC data suggest that hydroxy-Al-tannate existed dominantly as a separate phase. The high specific surface was due to the molecular association of hydroxy-Al-tannate and ethylene glycol monoethylether. Furthermore, the decrease in the CEC of the solid phase products after pretreatment with 0.2 M HCl was apparently due to the removal of pH-dependent charges of hydroxy-Al tannate complexes by the HCl treatment. The existence of hydroxy-Al-tannate as a separate phase bridging montmorillonite particles was verified by transmission electron microscopy and further substantiated by XRD and IR analyses.

The present study indicates that the mechanism of the perturbation of the formation of hydroxy-Al-montmorillonite complexes by organic acids in soils and sediments must vary with the nature of prevailing organic acids.

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