THE ELECTROPHORETIC MOBILITY OF IMOGOLITE AND ALLOPHANE IN THE PRESENCE OF INORGANIC ANIONS AND CITRATE*

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Abstract—The purpose of this study was to investigate bonding mechanisms of representative inorganic anions and citrate with imogolite and allophane using electrophoresis. The electrophoretic mobility (EM) of synthetic imogolite and allophanes with Al/Si molar ratios of 2.02, 1.64, and 1.26 was determined in 0.001 and 0.01 M sodium solutions. The highest point of zero mobility (PZM) values for imogolite and the highest point of zero charge (PZC) values for allophane occurred in the presence of ClO_4, NO_3, Br, I, and Cl. Below the PZM and PZC, Cl and I lowered the EM relative to the other anions but did not shift the PZM and PZC significantly. This indicates that Cl and I formed more outer-sphere complexes than the other ions. The EM of imogolite and allophane was negative at pH < 6 in 0.001 and 0.01 M NaF probably due to a phase change. We observed the formation of cryolite (Na_3AlF_6) with transmission electron microscopy (TEM) and X-ray diffraction (XRD) in the NaF systems at low pH. Conversely, phosphate at 0.001 and 0.01 M concentrations lowered both the PZM and the EM in imogolite and both the PZC and the EM in allophane compared with ClO_4. Phosphate-treated allophane had the same PZC as a synthetic amorphous aluminum phosphate. The PZM values of imogolite and allophane with 2:1 Al/Si in 0.0001 M Na-citrate were 10.9 and 5.9, respectively. At pH 7.3, Na-citrate lowered allophane EM more than it lowered imogolite EM relative to ClO_4.

The EM in $NaClO_4$ and Na_2SO_4 was reversible by forward- and back-titration with NaOH and $HClO_4$, indicated that ClO_4 and SO_4 were not specifically adsorbed. Chloride likely formed more outer-sphere complexes than ClO_4. Imogolite EM and allophane EM in dilute NaF and NaH_2PO_4 solutions were not reversible, indicating either surface inner-sphere complexes or surface precipitates of aluminum fluoride and amorphous aluminum phosphate-like materials on these minerals. Sulfate gave a lower EM than the monovalent anions, implying a greater tendency to form outer-sphere complexes. Citrate appeared to form inner-sphere complexes on both imogolite and allophane, but formation was concentration-dependent. The tendency of anions to form surface complexes with imogolite and allophane is consistent with the tendency of anions to form soluble aluminum complexes.

Key Words—Anion adsorption, Cryolite, Inner-sphere complex, Outer-sphere complex, Point of zero charge, Point of zero mobility, Specific adsorption, Surface complexation, Surface precipitation, Transmission electron microscopy.

INTRODUCTION

Imogolite and allophane are known to retain Cl, F, SO_4, PO_4, and other anions (Perrott *et al.*, 1976a, 1976b; Theng *et al.*, 1982; Clark and McBride, 1984; Parfitt, 1989, 1990; Su *et al.*, 1992); however, the chemical bonding between these anions and the functional groups of minerals is not well understood. It is necessary to develop a clear understanding of anion retention mechanisms because both imogolite and allophane carry net positive charge under acidic soil conditions. In addition, they both have high specific surface area, which makes them among the most important anion-sorbing materials in soils.

More Cl than ClO_4 sorption was observed on imogolite by Clark and McBride (1984). Su *et al.* (1992) found that the excess sorption of Cl could not be en-

tirely explained by simultaneous sorption of Na and Cl (salt absorption), and "specific" adsorption of Cl was proposed (Su *et al.*, 1992).

A ligand exchange mechanism has been suggested for F adsorption to allophane and imogolite in which F replaces surface OH groups (Wada, 1989; Parfitt, 1990). Because of this reaction, concentrated NaF is often added to soil as an indicator of reactive surface OH groups (Fieldes and Perrott, 1966; Perrott *et al.*, 1976a, 1976b). It is not known whether a ligand exchange or a dissolution-precipitation reaction is operative at F concentration > 0.001 M or if the same reaction occurs for both imogolite and allophane.

Allophanic subsoils retain SO_4 in excess of the positive charge determined by Cl adsorption (Parfitt, 1990). In comparison to soils containing mainly vermiculite and micas, much less SO_4 is leached from allophanic soils (Bolan *et al.*, 1988). Some researchers have suggested that an inner-sphere complex forms with goethite, hydrous alumina, and soils through a ligand ex-

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change reaction (Parfitt, 1978; Parfitt and Smart, 1977; Rajan, 1978; Martin and Smart, 1987; Zhang *et al.,* 1987); whereas, others have found evidence for outer-sphere complexation (Yates and Healy, 1975; Hansmann and Anderson, 1985; Ryden *et al.,* 1987; Zhang and Sparks, 1990) or precipitation of sulfate minerals such as alunite and basalunite (Xu *et al.,* 1991).

The phosphate reaction with allophane has been described either as discrete- or surface-precipitation (Veith and Sposito, 1977; Nanzyo, 1987) or as specific adsorption (Rajan, 1975a, 1975b; Rajan and Perrott, 1975; Yuan, 1980; Imai *et al.,* 1981). More phosphate is retained by allophane than imogolite (Theng *et al.,* 1982; Clark and McBride, 1984). It is not clear whether the sorption reaction differs between imogolite and allophane.

An organic carboxylate group was shown to be chemisorbed to allophane, but not to imogolite, by electron spin resonance spectra of a spin probe (Clark and McBride, 1984). Escudey *et al.* (1986) observed that citrate adsorption lowers the point of zero charge (PZC) of allophanic soil clays, supporting the existence of a chemisorbed species.

One means of investigating sorption mechanisms is to observe the mobility of individual particles suspended in an aqueous solution under an electric field by microelectrophoresis (Harsh and Xu, 1990). The electrophoretic mobility (EM) of a particle is determined by the electrostatic potential at the shear plane (the zeta potential), which is an imaginary plane separating the mobile particle and adsorbed molecules from the bulk fluid in which it is suspended (Hunter, 1981). Ions which form inner- and outer-sphere complexes are assumed to reside within the shear plane, whereas ions outside the plane do not contribute to the zeta potential. Thus, EM can serve as an indicator of the extent to which a given ion forms inner- and outer-sphere complexes. Furthermore, determination of the PZC can serve to distinguish between inner-sphere and outer-sphere complexation, because the former results in a shift in the PZC of a particle.

The specific objectives of this study are 1) to determine the relative extent of surface complexation between selected anions and imogolite and allophane as a function of mineral composition, mineral structure, pH, and anion charge, basicity, and concentration; 2) to distinguish between inner-sphere and outer-sphere complexation for a given anion on each surface; and 3) to distinguish between surface complexation and formation of a new solid phase for sulfate, phosphate, and fluoride reacted with each mineral.

MATERIALS AND METHODS

Synthesis of minerals

The imogolite and allophane used in the study were synthesized following the procedures described by Su

et al. (1992). The materials had Al/Si molar ratios of 2.01 for imogolite and 2.02, 1.64, and 1.26 for allophanes that were termed A2.0, A1.6, and A1.3, respectively.

An amorphous aluminum phosphate was synthesized by titrating a stirred mixture of 250 ml 1.0 M $AlCl_3$ plus 250 ml 1.0 M NaH_2PO_4 with 500 ml 1.0 M NaOH at a titrating rate of 5 ml min^{-1}. The pH of the suspension at the end point of titration was 4.1. The material was washed four times with and stored in 0.01 M NaCl.

Electrophoretic mobility

Suspensions containing imogolite or allophane were added to centrifuge tubes in 0.001 and 0.01 M solutions of Na_nA, where n represents the absolute charge of the anion A used. The solid concentration was 0.4 g liter^{-1} in 35 ml (use of solid concentration as low as 0.01 g liter^{-1} did not change the EM values). The suspension pH was adjusted using 0.1 M NaOH or 0.1 M H_nA, and allowed to equilibrate 24 hr. The addition of acid to adjust pH to a value near 3 in 0.001 M and 0.01 M solutions increased the final concentration to 0.0024 and 0.011 M, respectively, for all monovalent anions except fluoride, to 0.0053 and 0.014 M for phosphate, to 0.0053 and 0.011 M for sulfate, and to 0.015 and 0.033 M for fluoride. To achieve a final pH of 4.2 in 0.01 M NaF, 0.50 mmoles of HF were added to 0.07 mmoles of imogolite or allophane, giving a final concentration of 0.033 M for F. At pH >4, no significant increase in anion concentration occurred for any other anion. To avoid photochemical degradation, suspensions of NaBr and NaI were equilibrated in the dark.

The final pH of each suspension was determined after degassing under vacuum for 15 min to expel trapped air bubbles immediately before determining EM under ambient condition. The EM was determined with a Zeta Meter 3.0 equipped with a Zeiss DR stereomicroscope with 6.3× paired objective, 16× paired eyepiece, ocular micrometer, and in a Plexiglass cylindrical cell on a mirrored cell holder with a rod-type Pt-Ir cathode and cylinder-type Mo anode. In general, an average EM reading and its standard deviation were recorded after 30 particles were counted. The EM was also determined for imogolite and A2.0 as a function of NaF concentration at pH 6.0 and as a function of Na-citrate concentration at pH 7.3; both were adjusted with $HClO_4$ or NaOH. The amount of $HClO_4$ addition was negligible compared with that of F and citrate.

The reversibility of EM was checked by equilibrating samples 24 hr in 0.001 M $NaClO_4$, NaF, Na_2SO_4, or NaH_2PO_4 with 0.1 M $HClO_4$, HF, H_2SO_4, H_3PO_4, or NaOH to achieve pH values of 4 and 10.5 as starting points for perchlorate and sulfate, a pH value of 4 as a starting point for phosphate, and a pH value of 6.5 for fluoride. (At pH >6.5, no cryolite was found to form.) The suspensions were centrifuged, and super-
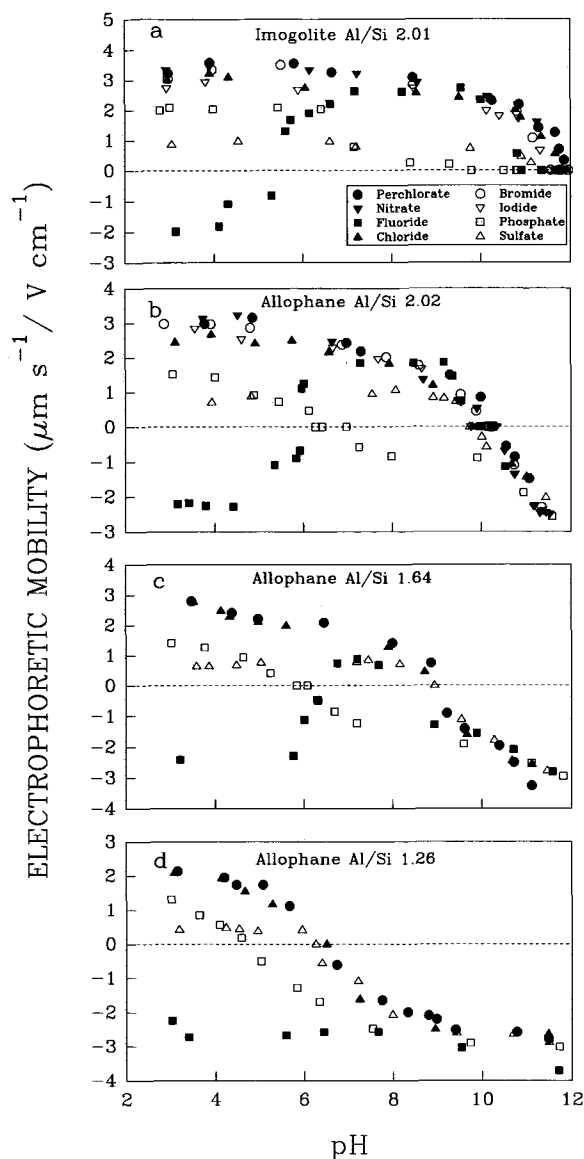
Figure 1.   Electrophoretic mobility of imogolite (a) and three allophanes (b, c, and d) in 0.001 M Na$_n$A (A denotes anion) as a function of pH and anion type.

Figure 2.   Electrophoretic mobility of imogolite (a) and three allophanes (b, c, and d) in 0.01 M Na$_n$A as a function of pH and anion type.

natant solutions decanted. The minerals were resuspended in the same electrolyte solutions, and the pH was increased from the starting pH 4 or 6.5 or decreased from the starting pH 10.5 by adding NaOH or the corresponding H$_n$A. The suspensions were equilibrated for 24 hr until the pH was steady and the EM was determined as above.

Transmission electron microscopy examination

Samples were mounted on copper grids with a Formvar coat, over which a thin carbon layer was deposited. Aliquots of the solid particles in distilled water were placed upon grids and dried prior to examination with a Hitachi H-600 microscope at 100 kV.
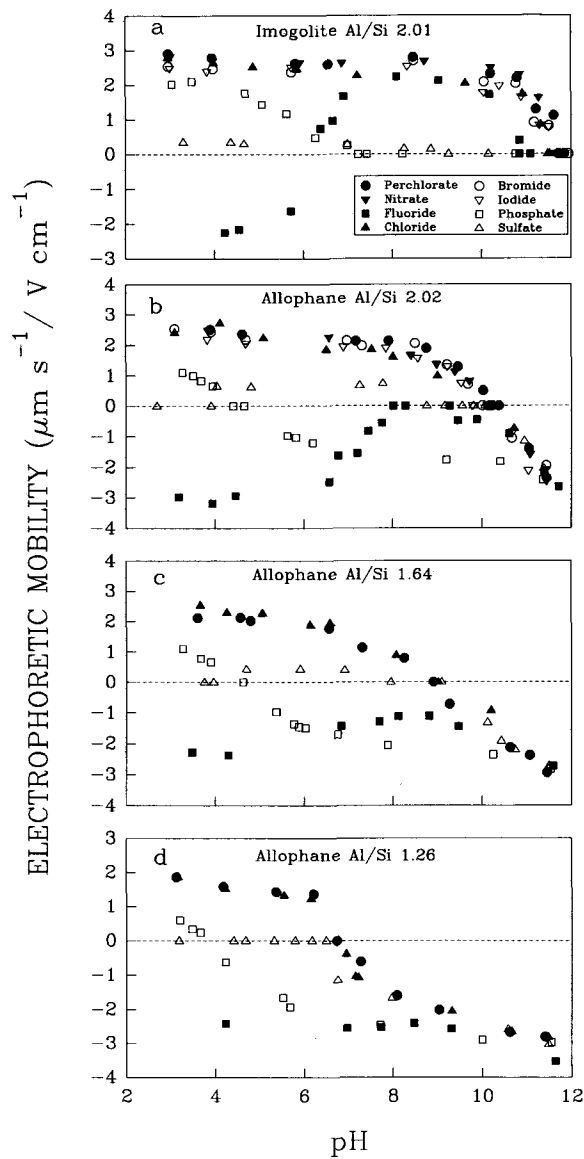
X-ray diffraction

X-ray diffraction patterns were obtained from oriented samples on glass slides with a CuKα X-ray source at 40 kV and with 15 mA using a Ni filter and a step scanning rate of 1° 2θ min^{-1}.

RESULTS

The EM of imogolite and three allophanes as a function of pH in 0.001 and 0.01 M NaClO$_4$, NaNO$_3$, NaF, NaCl, NaBr, NaI, Na$_2$SO$_4$, and NaH$_2$PO$_4$ is shown in Figures 1 and 2, respectively. The point of zero change (PZC) values are listed in Table 1. The PZC is defined

Table 1. Point of zero charge of imogolite and allophanes as affected by Al/Si molar ratio, anion type, and concentration.

Material Al/Si	Imogolite 2.01		Allophane 2.02		Allophane 1.64		Allophane 1.26	
Anion	10^{-3} M	10^{-2} M	10^{-3} M	10^{-2} M	10^{-3} M	10^{-2} M	10^{-3} M	10^{-2} M
ClO_4	None	None	10.3	10.2	9.0	8.9	6.5	6.7
NO_3	None	None	10.3	10.1	ND[1]	ND	ND	ND
F	5.4	6.1	5.9[2]	8.0	7.0[3]	None	None	None
Cl	None	None	9.8	10.1	8.8	8.8	6.7	6.7
Br	None	None	10.1	10.0	ND	ND	ND	ND
I	None	None	9.8	9.8	ND	ND	ND	ND
PO_4	None	None	7.0	4.5	5.9	4.6	4.7	3.8
SO_4	None	None	9.8	10.1	8.9	9.1	6.3	6.5

[1] Not determined.
[2] Also a second PZC of 10.
[3] Also a second PZC of 8.3.

as the pH at which the EM changes from positive to negative value. The point of zero mobility (PZM) is defined as the pH at which zero mobility occurs but no net opposite charge is obtained. The term PZM applies to imogolite in this study. The following features are notable: 1) imogolite had no PZC values with all anions except F at pH <6; 2) for monovalent anions except F, the PZC was not affected by ionic strength or ion size; 3) F generally lowered the PZC relative to monovalent anions and produced a lower PZC at 0.01 M than at 0.001 M; 4) only 0.01 and 0.001 M NaF shifted the PZC for imogolite, whereas both NaF and NaH_2PO_4 shifted the PZC for allophanes; 5) the PZC values of allophanes with all anions except F increased with increasing Al/Si molar ratio; 6) charge reversal

was observed for imogolite in both 0.001 and 0.01 M NaF and A2.0 and A1.6 in 0.001 M NaF solutions; 7) only negative EM was observed for A1.3 in either 0.001 or 0.01 M NaF or for A1.6 and A2.0 in 0.01 M NaF; and 8) increasing ionic strength generally lowered the PZC in the presence of phosphate and lowered the EM in the presence of monovalent ions.

Figure 3 shows that the EM of imogolite and A2.0 in 0.001 M $NaClO_4$ is reversible using 0.1 M $HClO_4$ or NaOH back-titration, respectively. Figure 4 shows that EM of imogolite and A2.0 in 0.001 M Na_2SO_4 is reversible using 0.1 M H_2SO_4 or NaOH back-titration, respectively.

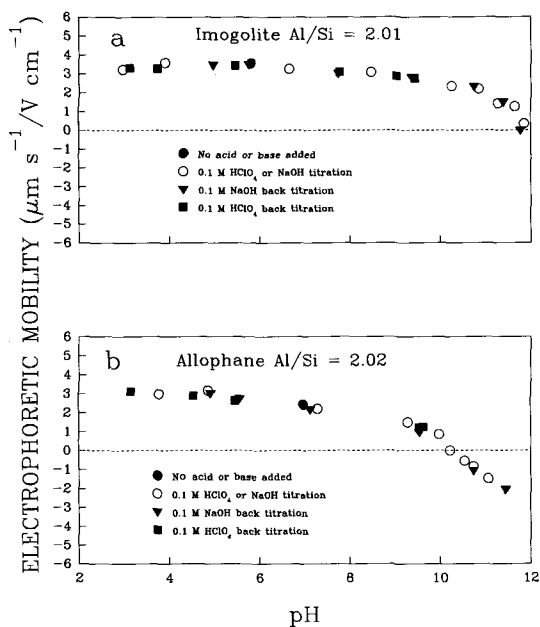Figure 5 shows the effect of NaF concentration on the EM of imogolite and A2.0. Zero EM was obtained

Figure 3. Electrophoretic mobility of a) imogolite and b) A2.0 in 0.001 M $NaClO_4$, as influenced by sequence of $HClO_4$ and NaOH addition.
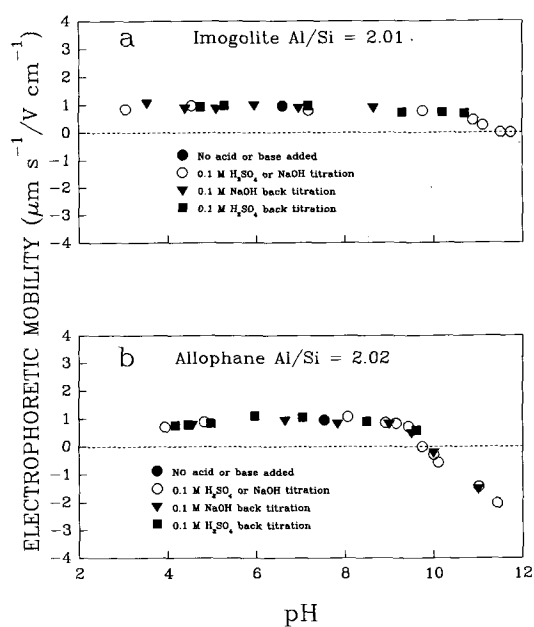
Figure 4. Electrophoretic mobility of a) imogolite and b) A2.0 in 0.001 M Na_2SO_4, as influenced by sequence of H_2SO_4 and NaOH addition.
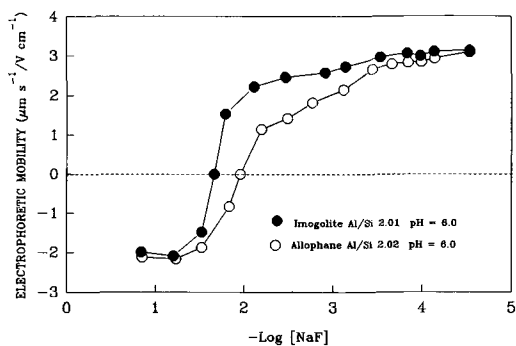
Figure 5. Electrophoretic mobility of a) imogolite and b) A2.0 at pH 6.0 as a function of NaF concentration.

Figure 6. TEM micrograph of cryolite formed from complete dissolution of A2.0 in 0.033 M F at pH 4.2.

in 0.022 and 0.011 M NaF for imogolite and A2.0, respectively. A new solid phase formed after a 24 hr treatment of imogolite and three allophanes in 0.01 M NaF at a final pH of 4.2. It had a monoclinic (pseudo-cubic) morphology with a diameter between 0.5 and 1.5 μm (Figure 6). It was not visible in water, indicating that its index of light refraction was very close to that of water. The precipitate, which showed a diameter greater than 0.5 μm under TEM, was isolated on a 0.2 μm Nuclepore polycarbonate filter for an XRD study. Strong XRD peaks at 1.94, 2.75, 3.88 Å and several small peaks at 2.32, 2.34, 1.57, 4.54, and 4.43 Å matched those of sodium aluminum fluoride (cryolite, Na_3AlF_6).

The morphology of imogolite and the three allophanes under the TEM was not affected in 0.01 M NaF at pH 8.1–9.3, implying the absence of a distinct separate phase such as cryolite; however, the effect of NaF concentration at pH 6.0 on the morphology of imogolite and A2.0 is readily apparent (Figure 7). Complete dissolution of the starting materials of imogolite and A2.0 was achieved in 0.14 M NaF at pH 6.0 after 24 hr, resulting in formation of cryolite (Figures 7a and 7c), but only partial dissolution of imogolite and A2.0 was achieved in 0.022 M and 0.011 M NaF at pH 6.0 (Figures 7b and 7d), respectively, as is indicated by the presence of imogolite (thread-like material) and cryolite (pseudo-cubic material) (Figure 7b) and the presence of both A2.0 (spherules <4 nm) and cryolite (Figure 7d). The irreversibility of the EM of imogolite and allophanes in 0.001 M NaF by 0.1 M HF or NaOH back titration is shown in Figure 8.

The EM of the synthetic amorphous aluminum phosphate (Al–P) was compared with that of clay-phosphate systems. Amorphous Al–P had a PZC of 5.6 (Figure 9) in 0.001 M NaCl. Mechanical mixtures of amorphous Al–P with imogolite and allophane had PZM or PZC values lower than those of either imogolite or allophane alone but higher than that of amorphous Al–P alone. The 0.01 M NaH_2PO_4 (pH 3.1)-treated allophane had a PZC identical to that of the amorphous Al–P (Figure 9b). In the micrographs,
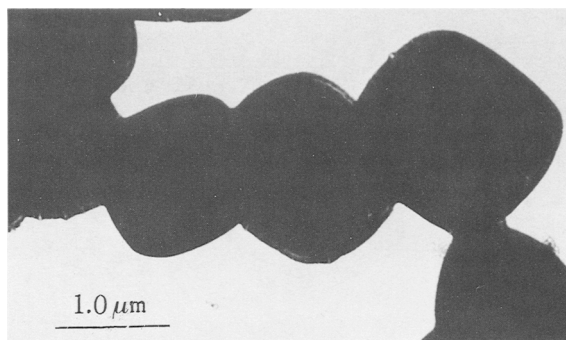
amorphous Al–P appeared as larger and darker particles compared with allophane (Figure 10A). The presence of 5% amorphous Al–P in imogolite or allophane was readily identified and 25% amorphous Al–P resulted in distinct differences in the morphology of imogolite and allophane (Figures 10B–10D). The irreversibility of the EM of imogolite and allophanes in 0.001 M NaH_2PO_4 by 0.1 M H_3PO_4 or NaOH back titration is shown in Figure 11.

Figure 12a shows non-negative EM of imogolite with a PZM of 10.9 and non-positive EM of A2.0 with a PZM of 5.9 in 10^{-4} M Na-citrate. The pH was adjusted with 0.1 M citric acid or NaOH. The effect of sodium citrate concentration at pH 7.3 (adjusted with 0.01 M $HClO_4$ and NaOH) on the EM of imogolite and A2.0 is shown in Figure 12b. A negative EM of imogolite occurred at a Na-citrate concentration above 0.0063 M at pH 7.3 (Figure 12b). At 0.01 M concentration at pH 7.3, the only other anion giving zero EM in imogolite was phosphate (Figure 2); however, phosphate never produced a negative EM, regardless of pH. At 0.001 M NaH_2PO_4 at pH 7.3, the EM of imogolite was still positive; whereas, in 0.001 M Na-citrate, imogolite EM was zero.

DISCUSSION

Monovalent anions

The effect of anions on EM is dependent upon the mineral structure and the chemical properties of the anions. If the anions reside outside the imogolite tubes and allophane spherules, then the differences in distribution about the shear plane, arising from differences in the size and basicity of the anions, should affect the EM. The range of the standard deviation of the EM values was large (0.05 to 0.4 μm s^{-1} V^{-1} cm). Although differences in the magnitude of EM as influenced by monovalent anions were not statistically significant, the PZM and PZC results do show some important trends.

For imogolite at the 0.001 and 0.01 M concentrations, the PZM values decreased in the order $ClO_4 \approx$
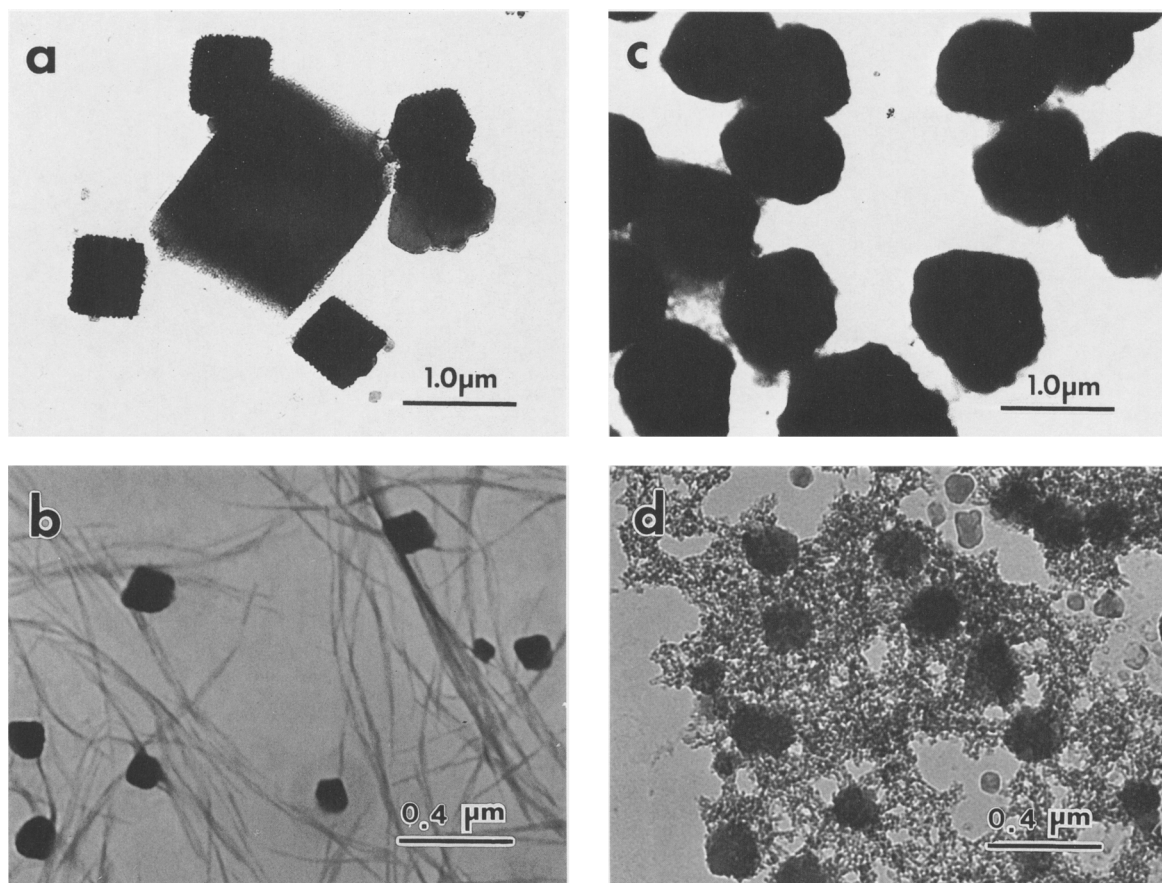
Figure 7. TEM micrographs of minerals formed at pH 6.0 adjusted with dilute $HClO_4$: a) particles of cryolite formed from complete dissolution of imogolite at pNaF = −0.85 with negative EM; b) imogolite (thread-like) and newly formed cryolite (pseudo-cubic) at pNaF = −1.66 with an apparent zero EM; c) newly formed cryolite from complete dissolution of A2.0 at pNaF = −0.84 with negative EM; and d) A2.0 (spherules <4 nm) and cryolite at pNaF = −1.96 with an apparent zero EM.

$NO_3 \approx Br \approx I \approx Cl \approx SO_4 > PO_4$. No negative EM value was observed with all the anions except F. The negative logarithm values for the first hydrolysis constant of oxyanions (pK_{b1}) of ClO_4, NO_3, SO_4, and PO_4 are 22.6, 16.9, 12.1, and 2.0, corresponding to non-basic, non-basic, weakly basic, and moderately basic anions, respectively (Wulfsberg, 1987), thus, the PZM decreased with increasing basicity of the anion. Of the monovalent anions, F, Cl, and I caused the lowest EM for imogolite below the PZM. This is consistent with adsorption data, which showed more Cl than ClO_4 was retained by imogolite (Clark and McBride, 1984). A lower imogolite EM at pH < PZM in 0.001 M NaCl and NaI than in 0.001 M $NaClO_4$ implies that Cl and I ions have a greater tendency to form outer-sphere complexes with imogolite.

The reversibility of imogolite and A2.0 EM in 0.001 M $NaClO_4$ and the lack of a shift in the PZM and PZC when the ionic strength was increased indicate that ClO_4 does not form inner-sphere complexes. It also shows that titrating imogolite and allophane to pH 10.5 and pH 3–4 does not alter surface properties sufficiently to cause irreversible changes in the EM.

No PZC was found for imogolite except with F. This contrasts with a PZC of 8.5–9.0 for a natural Japanese imogolite (Karube *et al.*, 1992). They attributed their results to the use of very dilute sample (0.005 g liter⁻¹); however, the impurities in the natural imogolite such as allophane, adsorbed citrate from extraction, and the structural defects could have resulted in the negative mobility.

Fluoride

The charge reversal of imogolite and allophanes (Figures 1 and 2) observed in the presence of NaF at low pH resulted from the precipitation of cryolite. A rapid fluoride-induced decomposition of allophane and its transformation to cryolite was demonstrated in concentrated NH_4F solutions by Birrell (1961). Our study
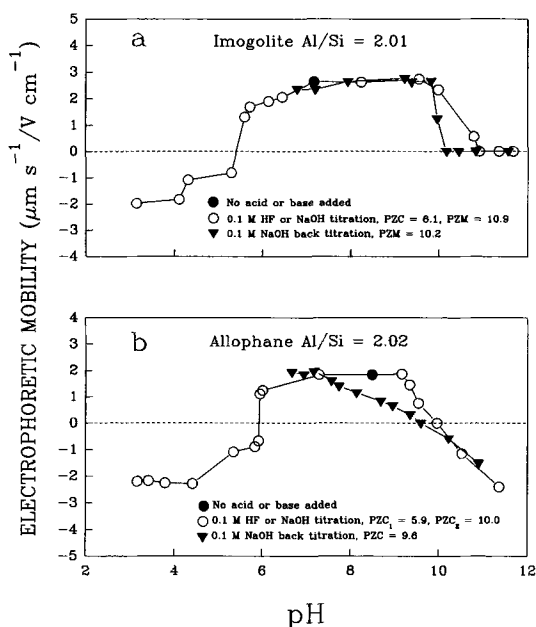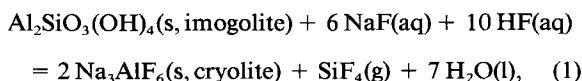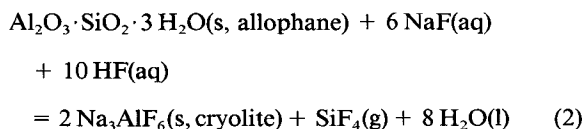
Figure 8. Electrophoretic mobility of a) imogolite and b) A2.0 in 0.001 M NaF as influenced by sequence of HF and NaOH addition.

Figure 9. Electrophoretic mobility of synthetic amorphous aluminum phosphate as influenced by the presence of a) imogolite and b) A2.0.

shows that the same reaction occurs in imogolite. The possible chemical reactions are:

$$Al_2SiO_3(OH)_4(s, \text{imogolite}) + 6\,NaF(aq) + 10\,HF(aq)$$

$$= 2\,Na_3AlF_6(s, \text{cryolite}) + SiF_4(g) + 7\,H_2O(l), \quad (1)$$

and

$$Al_2O_3 \cdot SiO_2 \cdot 3\,H_2O(s, \text{allophane}) + 6\,NaF(aq)$$

$$+ 10\,HF(aq)$$

$$= 2\,Na_3AlF_6(s, \text{cryolite}) + SiF_4(g) + 8\,H_2O(l) \quad (2)$$

for imogolite and A2.0, respectively. In A1.6 and A1.3, the same solid formed with NaF treatment at pH 4.2. It is evident that pH played an important role in the formation of cryolite in accordance with Reactions 1 and 2. The back titration of imogolite and A2.0 in 0.001 M NaF from a starting point of pH 6.5 caused a lower PZC relative to that obtained from the forward titration. This irreversibility could also be due to the formation of a discrete or surface precipitate, although this was not evident from TEM. It could also result from inner-sphere complexation of F with imogolite and allophane, and it is not possible to distinguish these two reactions with this data.

These results are relevant to the question of using 1 M NaF as a test for reactive surface hydroxyl groups in soils. Because high concentrations of F cause decomposition of both imogolite and allophane, even at high pH, the test is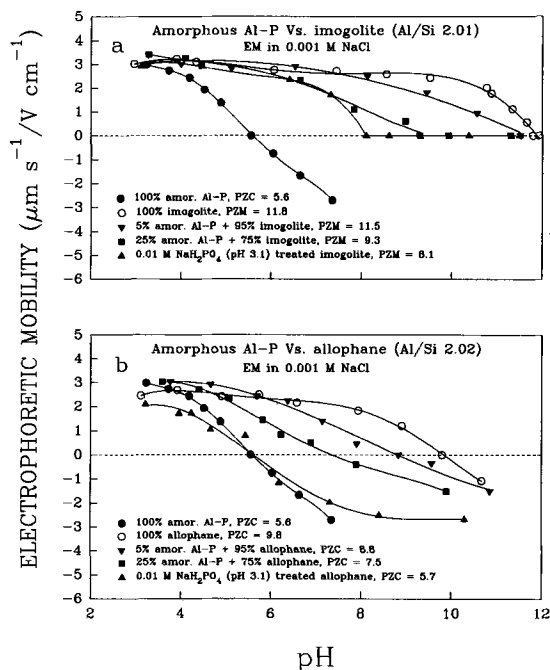 more indicative of "reactive Al and Si" than of "surface hydroxyls." Results from such a test should be considered accordingly. It should still serve as a qualitative test for poorly crystalline materials, such as imogolite and allophane, which are likely to decompose in the presence of NaF.

Sulfate

This study shows that sulfate lowers the EM of imogolite and allophanes relative to that of all the monovalent anions except fluoride. We conclude that SO_4 forms more surface complexes than do the monovalent anions. The reversibility of the EM of imogolite and A2.0 and 0.001 M Na_2SO_4 by back-titration with NaOH or H_2SO_4 (Figure 4), and the fact that the PZC is not lowered significantly by SO_4 implies that sulfate likely formed an outer-sphere complex with $Al\text{-}OH_2^+$ on imogolite or allophane.

The EM of imogolite in both 0.001 and 0.01 M Na_2SO_4 was lower than that at the same concentrations of NaH_2PO_4 at pH < 6.5 (Figures 1a and 2a). The same was also observed for the three allophanes, but at lower pHs (Figures 1b–1d and 2b–2d). This may be explained by the charge on the ions and ionic strength differences between the two systems. At lower pH, SO_4^{2-} is divalent and $H_2PO_4^-$ is monovalent. Thus, at the same molar concentrations, 0.001 M and 0.01 M, Na_2SO_4 solutions have higher ionic strength, 0.003 and 0.03, than those of NaH_2PO_4, 0.001 and 0.01, between pH 2 and 7. When pH is increased above neutrality, the phosphate charge and ionic strength increase. In this
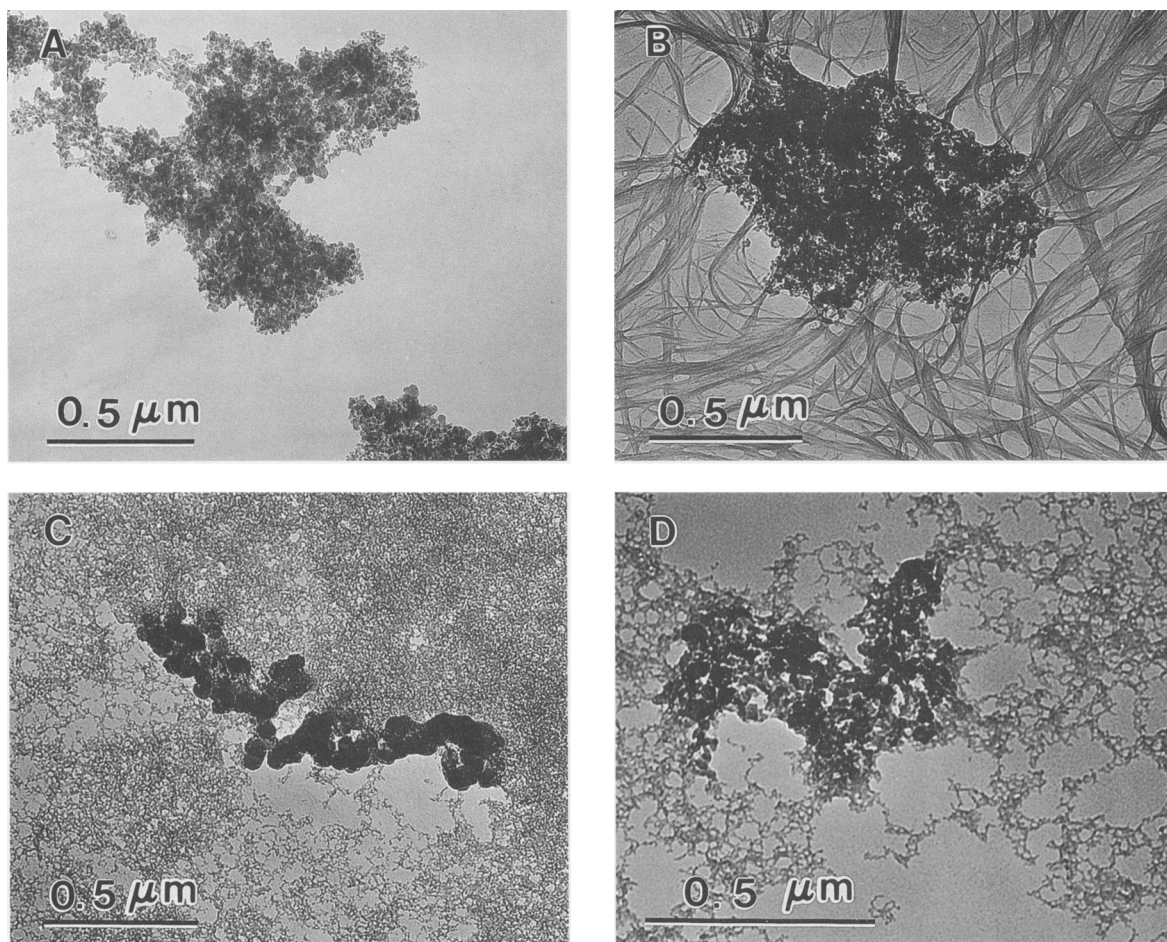
Figure 10. TEM micrographs of A) amorphous aluminum phosphate, B) 75% imogolite + 25% amorphous aluminum phosphate, C) 95% A2.0 + 5% amorphous aluminum phosphate, and D) 75% A2.0 + 25% amorphous aluminum phosphate.

case, the EM is lowered by phosphate relative to sulfate because of the tendency of phosphate to form inner-sphere complexes or surface precipitates.

Phosphate

Treatment of imogolite and the three allophanes in 0.001 and 0.01 M $NaH_2PO_4 + H_3PO_4$ did not result in other distinct solid phases observable by TEM; however, a surface precipitate smaller than the resolution limit of the TEM we achieved (about 2 nm) could have been formed. (The individual allophane particles were not resolved.) For example, Zachara *et al.* (1989) found that a zinc hydroxy carbonate surface precipitate was formed on $CaCo_3(s)$, but was not resolved by TEM up to 20,000× magnification.

The possibility of an aluminum phosphate surface precipitate is supported by two observations: 1) The EM of these materials in 0.001 M NaH_2PO_4 was irreversible with respect to pH (Figure 11); and 2) the phosphate-treated allophane had a PZC identical to that of synthetic amorphous aluminum phosphate

(Figure 9b). This study seems to support findings of Veith and Sposito (1977) and Nanzyo (1987), and the suggestions of Imai *et al.* (1981) and Parfitt (1989), that phosphate reacts with allophane to form X-ray amorphous aluminum phosphate. A coating of aluminum phosphate on gibbsite was also suggested by van Riemsdijk and Lyklema (1980) and van Riemsdijk *et al.* (1984) as a mechanism of phosphate reaction with gibbsite and acid sandy soils. Variscite was also reportedly formed in a laterite soil treated with monoammonium phosphate (Prabhudesai and Kadrekar, 1984).

Ligand exchange is considered to be the process involved in phosphate reaction with allophane based on the phenomenon of an increase in bathing solution pH and silicic acid concentration (Rajan, 1975a, 1975b). This was attributed to a release of surface hydroxyls during the exchange; however, the increase in solution pH may not be unique to a ligand exchange reaction. The dissolution of imogolite or allophane by phosphate and its transformation to amorphous aluminum phosphate can also result in an increase in pH and release
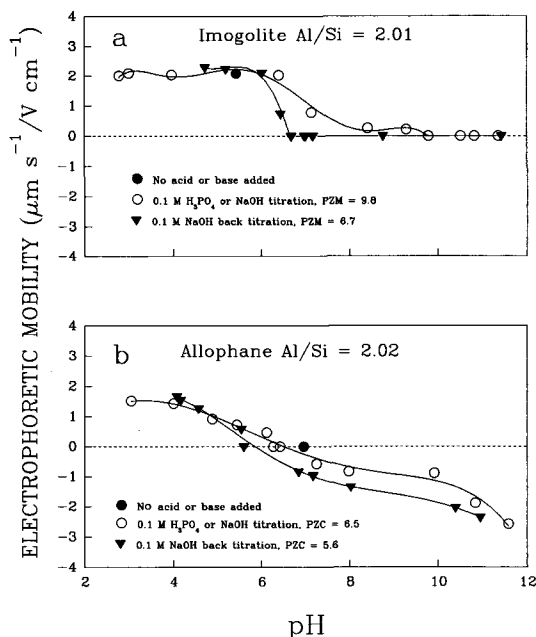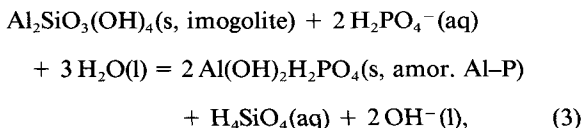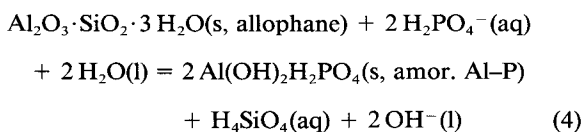
Figure 11. Electrophoretic mobility of a) imogolite and b) A2.0 in 0.001 M NaH$_2$PO$_4$, as influenced by sequence of H$_3$PO$_4$ and NaOH addition.

of silicic acid. In the following possible reactions, for example,

$$Al_2SiO_3(OH)_4(s, imogolite) + 2 H_2PO_4^-(aq)$$

$$+ 3 H_2O(l) = 2 Al(OH)_2H_2PO_4(s, amor. Al-P)$$

$$+ H_4SiO_4(aq) + 2 OH^-(l), \qquad (3)$$

and

$$Al_2O_3 \cdot SiO_2 \cdot 3 H_2O(s, allophane) + 2 H_2PO_4^-(aq)$$

$$+ 2 H_2O(l) = 2 Al(OH)_2H_2PO_4(s, amor. Al-P)$$

$$+ H_4SiO_4(aq) + 2 OH^-(l) \qquad (4)$$

one finds that hydroxide ions and silicic acid are products of the dissolution reactions.

Citrate

Escudey et al. (1986) suggested that the citrate ion, from a dithionite-citrate-bicarbonate (DCB) treatment to remove Fe oxides, lowered the PZC of allophanic clays. This study confirms Escudey et al.'s (1986) observation on both allophane and imogolite (Figure 12a) and supports Clark and McBride's (1984) conclusion that the organic-COOH group forms inner-sphere complexes with allophane as evidenced by the lowering of the PZC (Figure 12b). When citrate concentration exceeded 10^{-4} M, inner-sphere complexation also appeared to occur on imogolite. This contrasts with TEMPO-COOH ESR results, which showed no rigid limit spectrum for 10^{-4} M concentration (Clark and
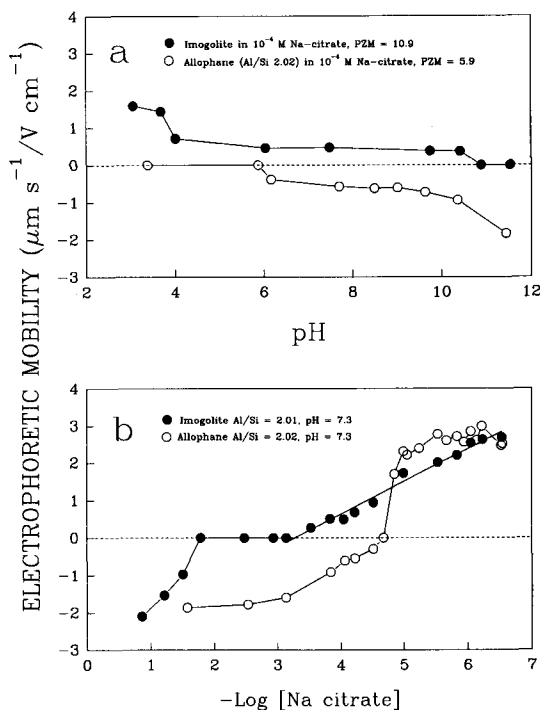

Figure 12. Electrophoretic mobility of a) imogolite and b) A2.0 at pH 7.3 as a function of Na-citrate concentration.

McBride, 1984); however, a preferential dissolution of Al from imogolite by citrate could also lower the PZC.

Our results (Figures 1, 2, and 12) suggest a mechanism for the flocculation rates observed by Horikawa and Hirose (1975) for imogolite and allophane in the presence of NaCl, Na$_2$SO$_4$, Na-citrate, and Na-laurylsulfate. Flocculation rate is a function of the distribution of ions about the surface of clay particles (Hunter, 1981). Flocculation rate increases as the PZC is approached. Citrate and laurylsulfate are strongly adsorbed anions that are attracted to positively charged surfaces of imogolite and allophane, lower the PZC, and, therefore, should increase flocculation rate.

Surface complexes vs. soluble complexes

In general, the tendency of anions to form surface complexes with imogolite and allophane is consistent with the tendency of anions to form soluble aluminum complexes. The citrate ion forms a soluble inner-sphere complex with the aluminum ion with a logarithmic value for the stability constant (log K_1) of 7.98 (I = 0.1 M) (Ohman and Sjoberg, 1983). The fluoride ion also forms inner-sphere complexes with the aluminum ion up to the maximum of octahedral coordination (AlF$_6^{3-}$) (Nordstrom and May, 1989). The log K value for the formation of AlF^{2+} is 7.0 (Smith and Martell, 1976), which is greater than a value of near 3 (I = 0.1 M, 18°C) for AlH$_2$PO$_4^{2+}$ (Bjerrum and Dahm, 1931), but similar to a value of near 7 for AlHPO$_4^+$ (Bohn

and Peech, 1969). The sulfate ion forms only outer-sphere complexes with metal ions (Garrels and Christ, 1965). Outer-sphere complexes result in log K values that change little across a number of metals with the same valence and roughly the same size (Langmuir, 1979), e.g., the log K values for MSO_4^+ when M = Y^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, etc., range from ~3.4 to 3.7 (Sillen and Martell, 1964). The log K values for the formation of $AlSO_4^+$ and $Al(SO_4)_2^-$ are 3.20 and 1.90 (Behr and Wendt, 1962). The discrepancy is accounted for by the fact that these ions (M) are larger (r ≈ 1.1 Å) than Al^{3+} (r ≈ 0.5 Å). The $AlSO_4^+$ complex is over 6000 times less stable than the AlF^{2+} complex. Other possible inorganic complexes with aluminum appear to be negligible.

SUMMARY AND CONCLUSIONS

The electrophoretic mobility of imogolite and allophane were affected by the charge and basicity of sorbed anions. The shift in PZM and PZC and the irreversibility of the EM of imogolite and allophane in dilute NaF and NaH_2PO_4 solutions suggest inner-sphere complexation or surface precipitation of amorphous Al phosphate and Al fluoride materials by PO_4 and F on these minerals. At low pH and high F concentration, complete dissolution of imogolite or allophanes occurred with formation of crystalline cryolite (Na_3AlF_6). Citrate appeared to form an inner-sphere complex with allophane and imogolite, but a higher concentration of citrate was required on imogolite.

The reversibility of EM of imogolite in 0.001 M Na_2SO_4 and $NaClO_4$ solutions suggested that inner-sphere complexes did not form with SO_4 or ClO_4 on imogolite and allophane. Outer-sphere complexation occurred to a greater degree with SO_4 than with ClO_4 on both imogolite and allophane. Chloride reduced the positive charge on both imogolite and allophane to a greater extent than did ClO_4, implying a greater tendency to form outer-sphere complexes. There was no evidence for inner-sphere complexation of Cl.

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