

ADSORPTION OF CATIONS ON IMOGOLITE AND THEIR EFFECT ON SURFACE CHARGE CHARACTERISTICS¹

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Abstract—Noncrystalline aluminosilicates termed allophane and imogolite are common constituents of spodosols, soils derived from volcanic ash, and many inceptisols. The surface charge characteristics of their synthetic analogues may be used to better understand their ion retention properties. In this study, we determined the point of zero salt effect (PZSE) by potentiometric titration of allophanes with Al/Si ratios of 1.12, 1.52, and 2.04 and of imogolite with an Al/Si ratio of 2.02. We also used microelectrophoresis to determine the point of zero charge (PZC) at the particle shear plane for the same materials in Cl solutions of Li, Na, Cs, and tetramethyl ammonium. The PZSE decreased with decreasing Al/Si ratio for the allophanes, but the imogolite PZSE was much lower than that of the allophane with 2.04 Al/Si. The PZC was always higher than the PZSE of the same material, especially for imogolite. The results are best explained if cations reside within the hollow tubes of imogolite. This conclusion is supported by a fluorescence study that showed that only quenchers smaller than the inner diameter of the imogolite tube could fully quench Ce-imogolite.

Key Words—Electrophoretic mobility, Microelectrophoresis, Noncrystalline aluminosilicates, Points of zero charge, Potentiometric titration, PZC, PZNPC, PZSE, Structural models, Surface charge, Surface complexation.

INTRODUCTION

Non- and para-crystalline aluminosilicates (allophanes and imogolite, respectively) occur in soils where weathering and high-solution silica and alumina levels combine to precipitate these metastable precursors of gibbsite, 1:1 phyllosilicates, and, possibly, 2:1 silicate clays. Due to their high specific surface area and almost ubiquitous occurrence, they are important participants in several soil reactions, including chemisorption of anions and transition metals, precipitation of aluminophosphates, ion exchange, and dissolution of aluminum. These reactions, and the potential use of imogolite as an industrial catalyst, have prompted an interest in the surface charge characteristics of allophane and imogolite.

Ion adsorption studies have been used to determine the total amount of positive and negative charge on synthetic and natural samples of imogolite and allophane as a function of pH (Perrott, 1977; Gonzales-Batista *et al.*, 1982; Theng, 1982; Clark and McBride, 1984; Wada, 1984; Su *et al.*, 1992). The electrophoretic mobility has also been determined as a function of pH and ionic strength for similar materials (Escudey and Galindo, 1983; Escudey *et al.*, 1986; Horikawa, 1975). Low exchange selectivities or nominal adsorption have been observed for larger cations such as cetylpyridi-

nium bromide (Greenland and Quirk, 1962) and paraquat (Knight and Tomlinson, 1967) on imogolite and for alkyl ammonium cations on allophane or soils containing both allophane and imogolite (Birrell, 1961; Wada and Tange, 1984).

Such data used alone give no information on the nature of the sites giving rise to surface charge or to the mechanism of ion adsorption; however, differences in the various points of zero charge can give such information. Sposito (1981) has shown that the point of zero charge (PZC) and point of zero salt effect (PZSE) are equal if

$$(\sigma_{IS} + \sigma_{OS})_{I1} = (\sigma_{IS} + \sigma_{OS})_{I2}$$

where σ_{IS} and σ_{OS} are the surface charges due to inner sphere and outer sphere complexes, respectively; and the subscripts I1 and I2 designate two different ionic strengths. This condition can be met if 1) no surface complexes form, 2) no inner sphere complexes form and cation and anion have roughly the same affinity for the surface, or 3) the solution concentration of an ion that contributes to σ_{IS} is held constant. A difference between the PZC and PZSE in aqueous NaCl, then, implies that either Na or Cl is specifically adsorbed or that they do not have the same affinity for the surface.

In this work, we focus on imogolite and allophanes that were synthesized to resemble the natural materials found in soils and pumice deposits (Farmer *et al.*, 1983; Wada *et al.*, 1979). Our objective is to determine the tendency for imogolite to form surface complexes with Na and/or Cl by comparing the PZSE determined by

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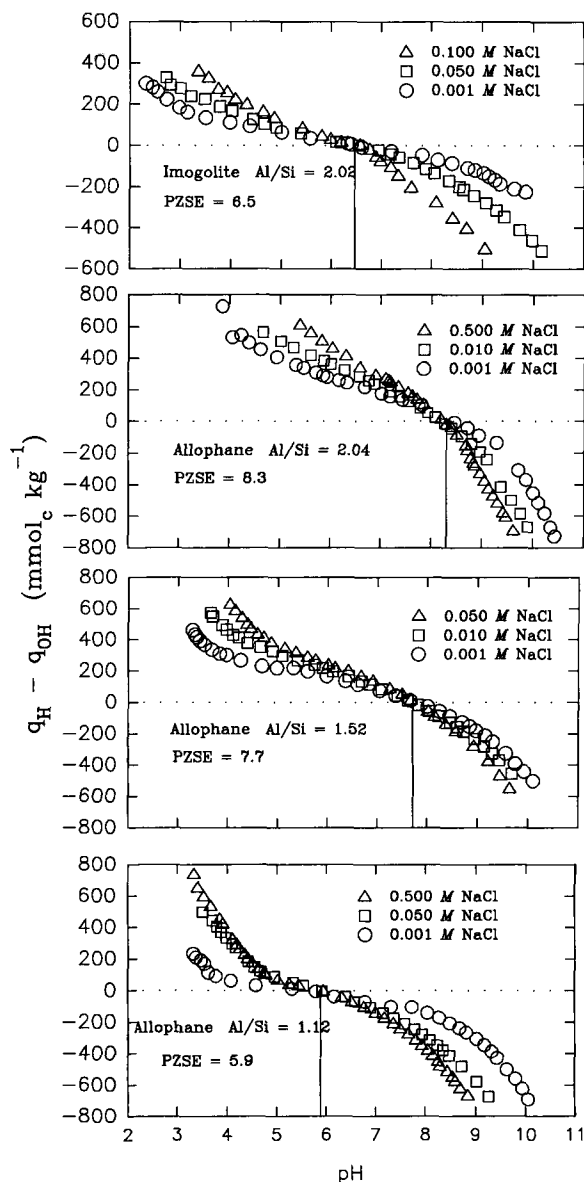


Figure 1. The point of zero salt effect for imogolite and allophanes of 2.04, 1.52, and 1.12 Al/Si molar ratio.

potentiometric titration with H^+ and OH^- and the PZC determined by microelectrophoresis. A potential mechanism for cation adsorption is then examined by fluorescence quenching of Ce(III) on imogolite.

MATERIALS AND METHODS

Materials synthesis

A modified procedure of Wada *et al.* (1979) described by Su *et al.* (1992) was used to prepare allophanes with Al/Si molar ratios of 1.12, 1.52, and 2.04. Imogolite was synthesized by the procedure of Farmer *et al.* (1983). The solids were dialyzed against distilled-

deionized water (DDW) until the electrolytic conductivity (EC) dropped below 0.003 dS m^{-1} . The resulting gels were stored in air-tight containers until used. The allophanes and imogolite were characterized by electron microscopy and diffraction, X-ray diffraction, chemical analysis, and Fourier transform infrared spectroscopy (FTIR). All conformed to characteristics found for these materials previously.

Electrophoretic mobility

Subsamples of the dialyzed suspensions were added to NaCl(aq) solutions to produce final bathing solution concentrations of 10^{-2} , 10^{-3} , and 10^{-4} M NaCl and a suspension density between 0.1 and 0.2 g kg^{-1} solution. (Use of suspension densities as low as 0.01 g kg^{-1} did not change the particle mobilities.) The suspension pH was adjusted to a range between 2 and 12 and allowed to equilibrate overnight. The long equilibration period was used to obtain a stable pH that did not drift during measurement and to ensure maximum dispersal of the particles. The final pH was recorded immediately before determining electrophoretic mobility (EM) with a Zeta Meter 3.0 equipped with a Zeiss DR stereomicroscope with $6.3\times$ paired objective, $16\times$ paired eyepiece, and ocular micrometer. The EM was determined in a Plexiglass cylindrical cell in a mirrored cell holder with a rod-type Pt-Ir cathode and cylinder-type Mo anode. A minimum of 20 particles were counted before recording an average reading, except in the high pH imogolite samples where gelation occurred and allowed only a few particles to be measured without thermal overturn.

In order to determine if overnight equilibration resulted in slow reactions such as dissolution, imogolite samples were adjusted to pH values of 5.65, 6.84, and 9.7. These samples were equilibrated for less than three minutes before determining EM. The pH values were redetermined after the mobility measurement and had dropped to 5.45, 6.20, and 9.36, respectively. There was no significant difference between the EM of samples subjected to the short and long equilibration times.

Potentiometric titration

A subsample of the stock suspension containing 0.100 g imogolite or allophane was added to a 0.5 liter potentiometric cell and the total volume of suspension was brought to 0.200 liter using "CO₂-free" (boiled, cooled under Ascarite trap) water. Final concentrations of 0.50, 0.10, 0.05, 0.01, and 0.001 M NaCl were obtained for the titrations.

To further remove CO₂, the suspension was bubbled for 30 min with N₂(g) that was first passed through an Ascarite trap and a NaCl solution of the same concentration as the sample. The suspension was titrated with 0.2 ml pulses of standardized 0.01 M NaOH or HCl and stirred for three minutes before a pH reading was recorded. A Metrohm Autotitrator and Orion Ross pH

and double junction reference electrodes were used to record volume delivered and pH, respectively. Identical readings were made on blank samples containing no mineral. The amount of H or OH adsorbed by the solid was calculated from the difference in volume of acid or base required to achieve the same pH in the sample as in the blank.

The PZSE is the crossover point determined by a plot of the titration curves at three or more NaCl concentrations. A set of three concentrations was chosen for each mineral based on the clarity of the crossover point or PZSE. A distinct crossover point required a large spread of NaCl concentrations in some samples.

Fluorescence quenching

Imogolite was saturated with Ce(III) by washing eight times with 10^{-4} M $\text{Ce}(\text{ClO}_4)_3$ at pH 5.5. The samples were equilibrated for 2 hr with each washing and centrifuged between each washing. Excess $\text{Ce}(\text{ClO}_4)_3$ was removed with ten H_2O washes and absence confirmed by the lack of fluorescence-detectable Ce ($\lambda_{\text{ex}} = 250$ nm and $\lambda_{\text{em}} = 355$ nm).

All fluorescence spectra were collected with a Perkin-Elmer LS-5B spectrofluorometer, interfaced to an MS-DOS computer. An aliquot of either Ce-imogolite or Na-imogolite was placed into a 1 cm quartz cuvette. An appropriate amount of either $\text{Cu}(\text{ClO}_4)_2$, acridine, 1-aminopyrene, or paraquat and a sufficient quantity of H_2O were added to bring the total volume to 3 ml. The total concentration of quenchers ranged from 0.00 to 19.33 mol m^{-3} for Cu^{2+} , 0.00 to $21.70 \text{ mmol m}^{-3}$ for acridine, 0.00 to $65.75 \text{ mmol m}^{-3}$ for 1-aminopyrene, and 0.00 to $64.81 \text{ mmol m}^{-3}$ for paraquat. The total imogolite concentration in each cuvette was $100 \text{ mg liter}^{-1}$. Preliminary analysis indicated that photo-physical equilibrium between each quencher and Ce-imogolite was reached in less than 1 min. All scans were collected after a reaction time of 5 min. Each sample was excited at a wavelength of 250 nm and fluorescence emission spectra were collected from 270 to 450 nm with the excitation and emission slits set at 5 nm.

RESULTS

The PZSEs of allophane and imogolite are shown in Figure 1. There was a decrease in the PZSE of the allophanes with decreasing Al/Si ratio. The decrease was not linear with respect to Al/Si ratio, as predicted by Parks (1967) for mixed oxide systems and as found by Schwarz *et al.* (1984) for heat-treated silica-alumina oxide suspensions.

The following four features are notable in the electrophoretic mobility curves (see Figure 2): 1) the PZC (as estimated by the point of zero mobility) increases with Al/Si ratio as expected for the allophanes and was higher for imogolite than for allophane with the same Al/Si ratio; 2) ionic strength (I) appears to have little effect on mobility at or above the PZSE; 3) no charge

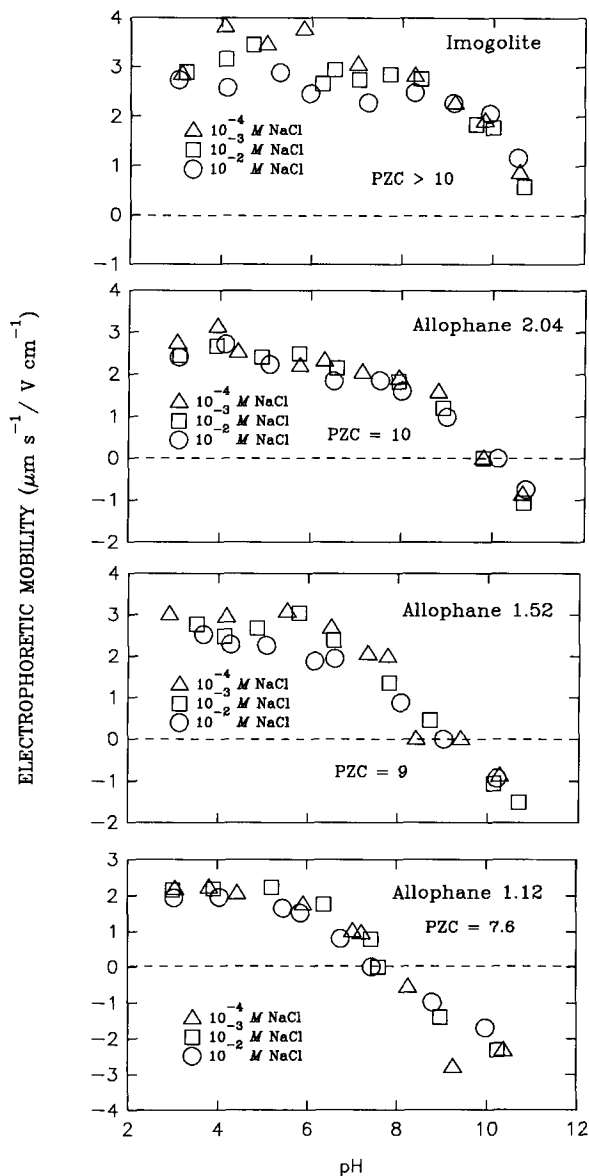


Figure 2. The electrophoretic mobility of imogolite and allophanes of 2.04, 1.52, and 1.12 Al/Si.

reversal was observed for imogolite; and 4) the PZC was always larger than the PZSE. This latter feature was most pronounced for the imogolite where the difference was more than 3.5 pH units.

Electrophoretic mobility was also determined for imogolite as a function of Cl concentration at pH 5.9 (Figure 3). This pH is below the PZSE (Figure 1) and the results reflect the influence of Cl adsorption on the electrophoretic mobility. The mobility becomes less positive with increasing Cl concentration.

The influence of the nature of the adsorbed cation at pH values, both above and below the PZSE of imogolite, is shown in Figure 4. The mobility did not

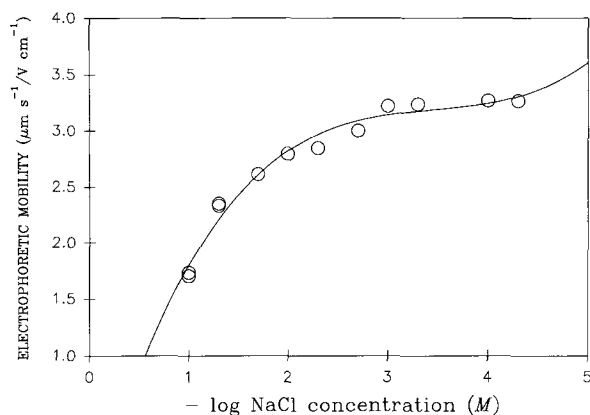


Figure 3. The electrophoretic mobility of imogolite at pH 5.9 as a function of NaCl concentration.

change regardless of size of the monovalent cation used. All cations had smaller radii than the imogolite tube. Similar results were found for Ca on imogolite (data not shown).

No fluorescence was observed for Na-imogolite. In the absence of Cu^{2+} , acridine, 1-aminopyrene, and paraquat, Ce-imogolite exhibited a single broad emission peak centered at approximately 355 nm (Figures 5–8). Acridine and 1-aminopyrene additions to Ce-imogolite also caused the appearance of strong emission peaks beginning at 380 and 390 nm, respectively. These peaks, due to emissions from acridine and 1-aminopyrene, were truncated from the spectra in Figures 6b and 7b. Whereas, additions of Cu^{2+} , acridine, aminopyrene, and paraquat resulted in decreases in the fluorescence emission from Ce(III) in Ce-imogolite, complete quenching of Ce-fluorescence was only observed in imogolite suspensions containing Cu^{2+} or acridine (Figures 5 and 6). The maximum quenching of Ce-fluorescence by 1-aminopyrene and paraquat oc-

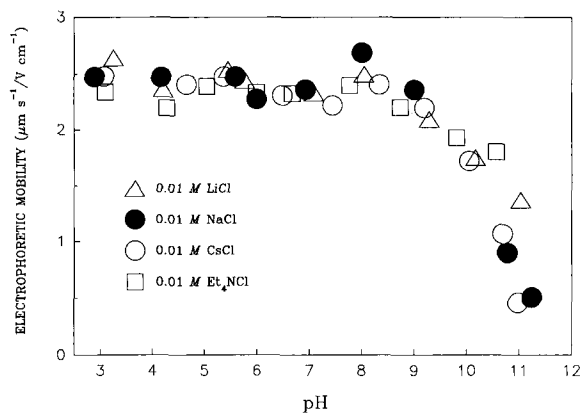


Figure 4. The electrophoretic mobility of imogolite in the presence of 10 mol m^{-3} Cl solutions of Li, Na, Cs, and tetraethylammonium.

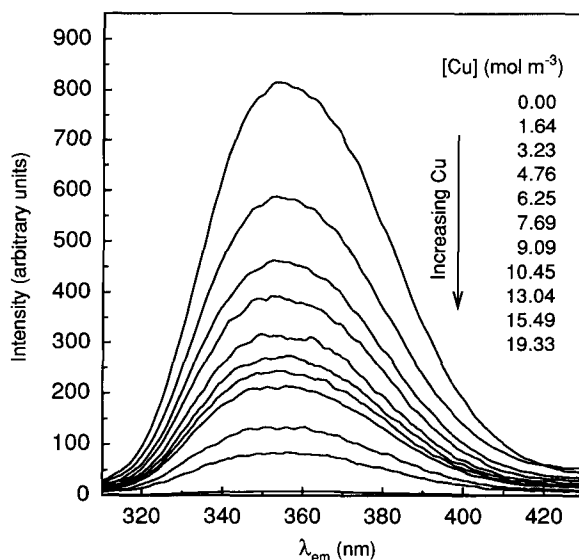


Figure 5. Effect of $\text{Cu}(\text{ClO}_4)_2$ on Ce-fluorescence from Ce-imogolite.

curred at quencher concentrations of 41.84 and 45.75 mmol m^{-3} , respectively. Greater concentrations of 1-aminopyrene and paraquat did not cause additional reductions in Ce-fluorescence (Figures 7 and 8). All four quenchers were able to quench Ce completely in $\text{Ce}(\text{ClO}_4)_3$ and Ce-hectorite systems.

DISCUSSION

Nature of titratable sites in imogolite and allophane

Kuo and Yen (1988) have shown that prediction of the PZSE (assuming that the PZSE is equivalent to the point of zero net proton charge or PZNPC) must be based on actual titration curves which show the sensitivity of charge to a change in pH. They also point out that the surface charge density must be known for the component hydrous oxides and it must be assumed that there is no interaction among sites. Additionally, it must be assumed that H is only consumed in surface-charging reactions and that neither Na nor Cl is "specifically adsorbed," limiting the free adsorption of H at a particular site (Parker *et al.*, 1979). Although titration curves for hydrous alumina and silica are available, the surface areas of the Al and Si components in allophane and imogolite are not known, nor is the acidity of the Si-OH sites. In addition, the assumption of noninteraction is probably not valid; ion exchange between H and Na on permanent charge sites occurs in the allophanes with Al/Si < 2 (Su *et al.*, 1992); and specific adsorption of Na and/or Cl is possible (Su *et al.*, 1992).

Reinforcing the inference that the PZSE is not a simple function of Al/Si ratio for noncrystalline aluminosilicates is the fact that the PZSE of imogolite is 2

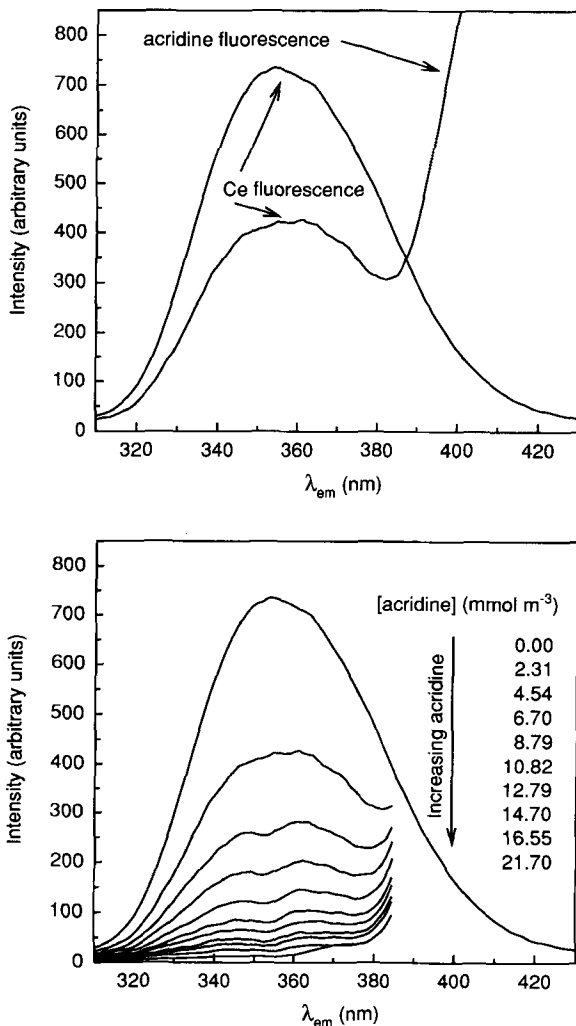


Figure 6. Effect of acridine on a) Ce- and acridine-fluorescence and b) Ce-fluorescence from Ce-imogolite.

pH units less than that of the allophane with the same Al/Si ratio. It cannot arise from permanent charge brought about by the presence of tetrahedral Al in 2:1 allophane, because charge from isomorphous substitution does not affect the PZSE (Sposito, 1981); however, this may be due to other structural differences between imogolite and the 2.04 Al/Si allophane.

The widely accepted structure of imogolite and allophane of 2:1 Al/Si is that of an outer gibbsite-like sheet pulled into a cylinder and sphere, respectively, by silica coordinated to the inside of the sheet (Cradwick *et al.*, 1972; van Reeuwijk and de Villiers, 1970). Nuclear magnetic resonance of ^{29}Si in noncrystalline aluminosilicates has shown that both synthetic and natural materials consist of imogolite-like structures in which the Si is directly bound to OH groups and allophane structures in which the Si is more fully polymerized and bound through oxygen to either Al or Si

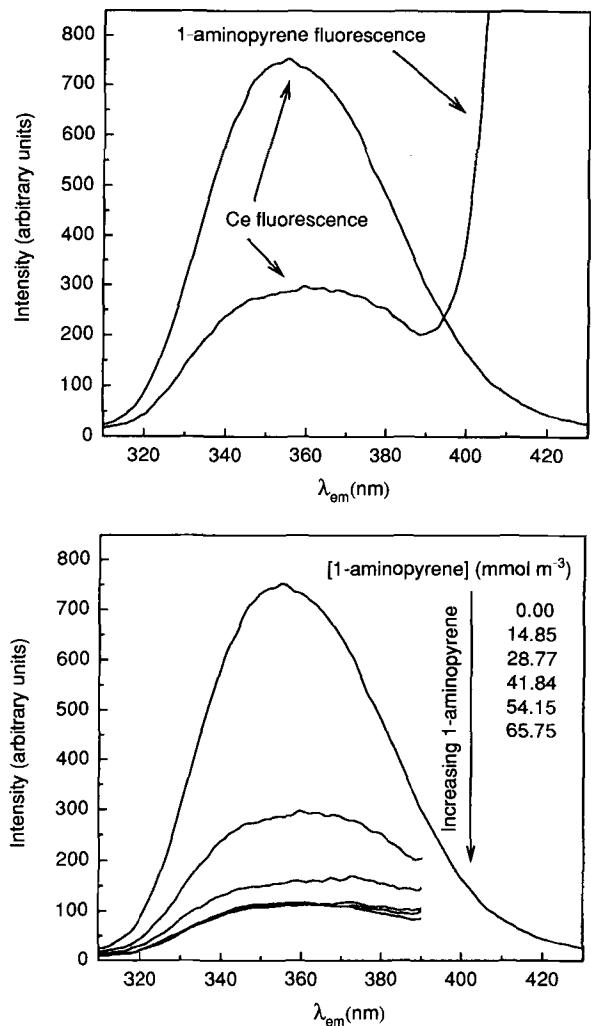


Figure 7. Effect of 1-aminopyrene on a) Ce- and 1-aminopyrene-fluorescence and b) Ce-fluorescence from Ce-imogolite.

(Wilson *et al.*, 1986; Goodman *et al.*, 1985). As a result of the lack of Si-O polymerization, imogolite should have more Si-OH sites capable of adsorbing or losing protons and, in the terminology of Kuo and Yen (1988), show greater "sensitivity" to pH changes. The reactivity of the Si-OH groups in imogolite is not known, but the lower PZSE of imogolite than the 2.04 allophane, and the fact that Na adsorption is greater in imogolite than in allophane at high pH (Su *et al.*, 1992), implies some groups are titratable in the pH range 2–12. It is possible that reactive Si-OH groups are associated with defects in the imogolite structure. In any case, the model of Cradwick *et al.* (1972) suggests that negatively charged sites will be present inside the imogolite tubes.

The location of adsorbed cations on imogolite

The PZC of a solid is greater than the PZSE when the adsorbing cation forms more surface complexes

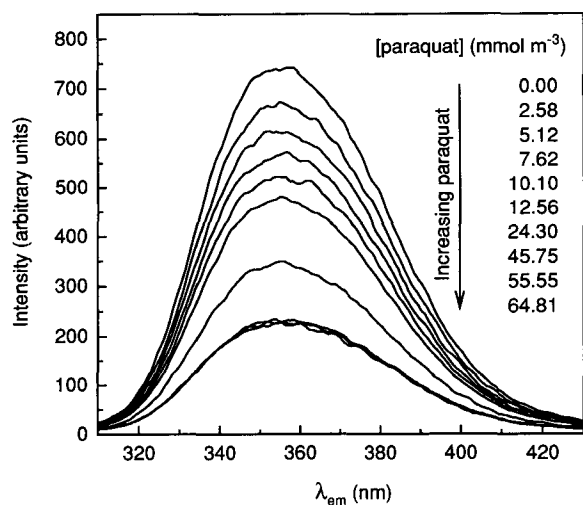


Figure 8. Effect of paraquat on Ce-fluorescence from Ce-imogolite.

than the anion (Sposito, 1981). If Na ions were to move inside the imogolite tubes or allophane spherules, they would reside within the shear plane and increase the electrophoretic mobility.

The lack of an ionic strength effect on electrophoretic mobility of imogolite over much of the pH range is consistent with the hypothesis that Na ions reside within the imogolite tubes. In most oxide systems, an indifferent ion such as Na may reside within or outside the shear plane. As the ion concentration increases, more ions tend to penetrate the shear plane, reducing the magnitude of the electrostatic potential at the shear plane and, hence, the magnitude of the electrophoretic mobility. If most of the Na ions on imogolite reside within the tubes, increasing their concentration in solution will have little effect on the potential at the shear plane.

At pHs well below the PZSE of imogolite, Cl adsorption should dominate and the mobility should become more negative with increasing Cl concentration as more Cl moves within the shear plane. The results in Figure 4 clearly support this hypothesis. This also implies that much of the Cl must reside outside the imogolite interior where it may influence the shear plane potential (aka, the zeta potential).

In addition to a lack of ionic strength effects, if the cations reside within the hollow imogolite cylinders, the nature of the cation should have little or no influence on electrophoretic mobility as long as the cation is small enough to fit within the 1 nm interior diameter. This was found to be the case on imogolite for Li, Na, Cs, and tetraethylammonium, which differ in size and mass but are all small enough to fit easily into the imogolite cavity (Figure 4).

Four anomalous charge characteristics of imogolite—a higher PZC than that of 2:1 allophane; a higher

PZC than PZSE; and lack of specific cation effects on the electrophoretic mobility—may be explained if cations reside inside the imogolite tubes. The fluorescence emission spectra show that this is almost certainly the case. Copper ions, which can move freely in both intratubular and intertubular pores of imogolite, quench all of the Ce(III). Acridine, which has a molecular diameter of about 0.8 nm, may move freely within imogolite tubes (inner diameter \approx 1 nm), but will be restricted from intertubular pores if hexagonal close-packing is assumed ($d \approx$ 0.4 nm). Thus, complete quenching by acridine implies that Ce is not located in pores among tubes. On the other hand, the failure of 1-aminopyrene and paraquat ($d >$ 1 nm) to quench all the fluorescence shows that some Ce(III) must be unavailable to the quenching agent and, therefore, inside the tube. It is possible that all the Ce(III) is located inside the tube but is partially quenched because it is located at tube edges or is quenched by photophysical processes that do not involve molecular collisions.

Intratubal adsorption of cations does not explain why the electrophoretic mobility of imogolite remains positive well above the PZNPC of pure aluminum hydroxide. It is also not explained by specific adsorption of Na, because Su *et al.* (1992) have shown that Na adsorption above pH 8.4 is equal to the proton charge on imogolite. The anomalous PZC as well as the presence of Cl adsorption well above the PZSE (Su *et al.*, 1992) could be explained by the existence of permanent positive charge on imogolite. Permanent positive charge would arise from structural features and not be affected by solution composition, such as the negative charge on 2:1 phyllosilicate clays. Currently, there is no microscopic evidence for permanent charge in imogolite nor is this hypothesis consistent with the accepted structural models of imogolite.

SUMMARY AND CONCLUSIONS

The PZSEs of the allophanes decreased with decreasing Al/Si ratio, but the relation was not linear. Imogolite had a PZSE far below that of allophane of the same Al/Si ratio. The PZCs of the allophanes and imogolite were all significantly higher than the PZSEs, especially for the imogolite. Significant ionic strength effects on imogolite mobility were only evident below the PZSE and no specific cation effect was evident. These results are partially explained if some of the Si-OH groups within the imogolite tube are titratable and Na ions are adsorbed inside the tubes. The fact that Ce(III) on imogolite cannot be entirely quenched by molecules with diameters larger than the tubes confirms that some cations do reside within imogolite.

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