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SURFACE CHARGE CHARACTERISTICS OF AMORPHOUS ALUMINOSILICATES

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Abstract—The surface charge characteristics of a range of synthetic amorphous aluminosilicates, hydrous alumina, hydrous silica and two allophanic soil clays were determined by the retention of Na^+ and Cl^- as counter-ions from 0.1 M NaCl solution. In the pH range investigated (3–9), only negative charges could be detected in the hydrous silica and the most siliceous aluminosilicate [Al/(Al + Si) = 0.29], and only positive charges were detected in the hydrous alumina; whereas both positive and negative charges were detected in the more aluminous aluminosilicates and the soil allophanes. In all cases, the surface charges were pH-dependent and in the aluminosilicate series negative charge decreased and positive charge increased with Al/(Al + Si). Consequently, the point of zero charge increased with Al/(Al + Si).

The charge characteristics of the amorphous aluminosilicates could be explained by current models of their structure. Negative charge can be attributed to isomorphous substitution of Al for Si in the silicate structure and to the dissociation of silanol groups in structural and adsorbed silicate. Positive charge is attributed to protonation of hydroxy-aluminum species occupying cation exchange sites.

INTRODUCTION

In contrast to soils with a clay mineralogy dominated by crystalline layer silicates, soils containing the amorphous clay allophane have cation exchange capacity (CEC) values which are strongly dependent on the details of the measurement method. The concentration, type of cation and pH of the saturating solution and the washing method all have a marked influence on the measured CEC (Wada and Harward, 1974). Also, unlike the crystalline layer silicates, which have very little positive charge, allophane possesses comparable amounts of positive and negative charges in the pH range 3–9 and these charges are pH-dependent (Fields and Schofield, 1960; Iimura, 1961).

Because of the difficulty of obtaining soil allophane free from contaminants such as crystalline clay minerals, soil organic matter and iron oxides without using treatments which could alter surface properties, much of the progress that has been made in understanding the surface charge characteristics of non-crystalline soil clays has been obtained from the study of synthetic amorphous aluminosilicates. Milliken *et al.* (1950) found that in synthetic amorphous aluminosilicates with up to 30% Al_2O_3, one equivalent of CEC was present for each mole of Al in the structure. This was confirmed by Tamele (1950) and attributed to the presence of tetrahedral Al. Leonard *et al.* (1964) confirmed the presence of tetrahedral Al by X-ray fluorescence measurements. CEC variations with aluminosilicate composition have been explained by the models of Cloos *et al.* (1969) and van Reeuwijk and de Villiers (1970), which consider amorphous aluminosilicates to consist of an aluminosilicate phase with permanent negative charge arising from isomorphous substitution of Al for Si, and a hydroxy-aluminium phase with pH-dependent positive charge.

Recently, Fey and le Roux (1976) reported results of surface charge measurements at several pH values on sesquioxidic soil clays and three synthetic amorphous aluminosilicates with compositions corresponding to 41, 53 and 65% $Al_2O_3/(Al_2O_3 + SiO_2)$. They used a technique which does not require a washing step for the removal of excess salt before the replacement of the index ions. This is desirable as it prevents the loss of the index ions by hydrolysis which is a problem with amorphous aluminosilicates (Wada and Harada, 1969) and was usually ignored in previous work. The present paper reports the results of the measurement, using similar methods, of pH-dependent positive and negative charges in synthetic aluminosilicates with a wider compositional range. The surface charge characteristics of hydrous oxides of aluminium and silicon and of two soil clays containing allophane were also determined.

MATERIALS AND METHODS

Pure synthetic aluminosilicates were prepared by the simultaneous hydrolysis of aluminium isopropoxide and methyl silicate as described by Rajan and Perrott (1975). Hydrous alumina and silica were prepared by the separate hydrolysis of the respective alkoxides.

Clay fractions ($<2\,\mu m$) from the subsoil of Waihi sandy loam (Vitric Andept), which is derived from rhyolitic volcanic ash, and from an allophanic bed in the Hamilton Ash Formation at Te Akatea (Tonkin, 1970) were obtained by gravitational sedimen-

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tation after ultrasonic dispersion of the soil samples. Treatments with H_2O_2, Na_2CO_3 and citrate–dithionite commonly used in the separation of soil clays were omitted because of possible effects on surface charge determining species. After concentration by flocculation with $MgCl_2$ the clay suspensions were dialyzed until free from Cl^- and freeze-dried.

The synthetic samples and soil clays were characterized by differential thermal analysis, X-ray powder diffraction, infrared absorption spectroscopy, electron microscopy and electron diffraction. Elemental composition was determined by the method of Boar and Ingram (1970) and BET surface areas determined by nitrogen sorption, using an automatic surface area analyser (Carlo-Erba Sorptomatic Series 1800).

A modified procedure based on that of Schofield (1949), and similar to the methods of Wada and Harada (1969) and Chichester *et al.* (1970), was used to determine surface charge characteristics. Approximately 0.2 g of each sample was washed three times with 1 M NaCl followed by three washings with 0.1 M NaCl. Suspensions in 0.1 M NaCl were adjusted to the desired pH value, which was then maintained for 1 hr, by addition of 0.1 M HCl or 0.1 M NaOH controlled by an automatic titrator (Radiometer-Copenhagen) used in the pH-stat mode. The samples were then transferred to 15 ml conical centrifuge tubes and washed seven more times with 0.1 M NaCl adjusted to the required pH value. Because of the strong buffering capacity of many of the samples studied, the pH value of the final supernatant often differed from the required pH value. In a few cases, this difference was as much as 1.5 pH units. The final pH value was therefore taken as the pH value of the surface charge measurement. After decanting the final wash solution, the centrifuge tubes were immediately stoppered and weighed to enable calculation of the entrained NaCl solution.

The total Na^+ and Cl^- (exchangeable plus entrained) was displaced by five 10-ml washes with 0.05 M $Ca(NO_3)_2$ and the washes combined and made up to 100 ml for analysis. Sodium was determined by atomic absorption spectrophotometry and chloride by the colorimetric mercuric thiocyanate method (Florence and Farrer, 1971). The exchangeable Na^+ and Cl^- were obtained after subtraction of the gravimetrically determined NaCl in the entrained NaCl solution.

After displacement of Na^+ and Cl^-, the centrifuge tubes were dried at 105°C to constant weight and the oven dry sample weight calculated by subtracting the dry weight of the tube and entrained $Ca(NO_3)_2$.

RESULTS

The results of the analysis and characterization of the synthetic samples and soil clays are given in Table 1. The surface charge characteristics of the synthetic samples and the soil clays are shown in Figures 1 and 2, respectively.

The point of zero charge (PZC) pH values, determined from plots of net surface charge vs pH, are given in Figure 3. As can be seen from Figure 1, sample A [Al/(Al + Si) = 0.29] did not have a PZC in the pH range investigated.

Hydrous silica has pH-dependent negative charge at pH values above about 6 and no positive charge was detected in the pH range used (3–9). Hydrous alumina, on the other hand, has only pH-dependent positive charge in this pH range.

With the exception of sample A, in which no positive charges could be detected, the amorphous aluminosilicates have both positive and negative charges. These charges are pH-dependent, with the positive charges decreasing and the negative charges increasing with pH. The magnitude of the positive charges increases with increasing mole fraction of aluminium [Al/(Al + Si)] in the aluminosilicate and hence the PZC pH value increases with Al/(Al + Si). The plot of PZC vs Al/(Al + Si) given in Figure 3 follows

Table 1. Characteristics of synthetic aluminosilicates, hydrous oxides and soil clays

	Organic C (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	$\frac{Al}{Al + Si}$ (molar ratio)	Surface area (m^2/g)	Mineralogy
Hydrous SiO_2		95.4	0	0	0	—	Amorphous
A		61.0	21.5	0	0.29	190	Amorphous
B		47.6	32.8	0	0.45	272	Amorphous
C		38.5	41.0	0	0.56	278	Amorphous
D		31.2	47.8	0	0.64	357	Amorphous
E		11.7	66.0	0	0.87	264	Amorphous + trace of pseudoboehmite
Hydrous Al_2O_3		0	72.9	0	1.00	231	Bayerite + pseudoboehmite
Te Akatea	0.8	32.7	38.7	3.9	0.58	—	Allophane + trace of imogolite
Waihi	2.1	33.1	33.6	6.9	0.54	181	Allophane + small amount of imogolite

Chemical analysis and surface area are expressed on oven dry (105°C) basis.

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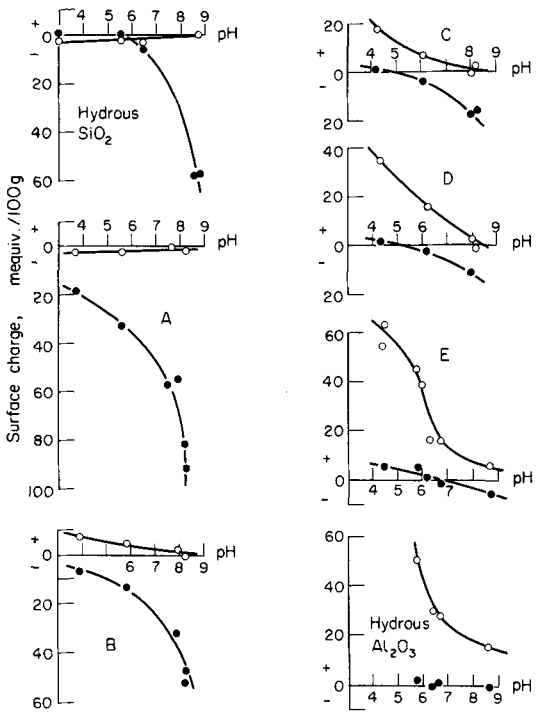


Fig. 1. Surface charge variations with pH for synthetic aluminosilicates and hydrous oxides. (○—positive charges, ●—negative charges.)

closely the theoretical compsition dependence of PZC of SiO_2–Al_2O_3 co-precipitates derived by Parks (1967). The discontinuity in the theoretical composition dependence of PZC arises from the assumption that for Al/(Al + Si) < 0.4 all the Al is present in tetrahedral form, whereas for Al/(Al + Si) > 0.4 all the Al is present in octahedral form.

The aluminosilicates do not exhibit the constant negative charge in the pH range 4–7 which is observed with the crystalline clay minerals and attributed to permanent charge arising from isomorphous substitutions in the crystal structure (Fieldes and Schofield, 1960). However, both A and B have negative charges at pH 4 which has been used by Hussain and Kyuma (1970) as a convenient arbitrary measure of permanent charge.

Although the magnitudes of the positive and negative charges on the allophanic soil clays are larger than the charges on the synthetic aluminosilicate C,

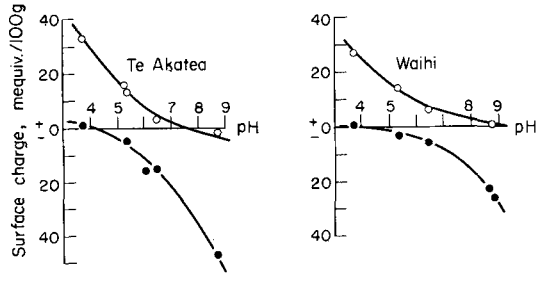


Fig. 2. Surface charge variations with pH for soil clays. (Symbols as in Fig. 1.)

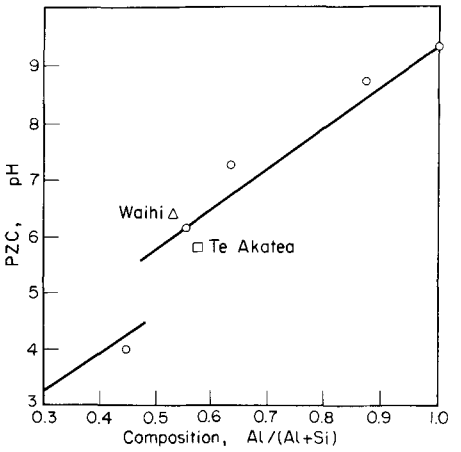


Fig. 3. Effect of composition on PZC. ○, △, □ experimental points for synthetic samples and soil clays, respectively; ——, theoretical (Parks, 1967).

which has a similar Al/(Al + Si) ratio, the variation of charges with pH is the same. The PZC values of these soil clays is also close to the value expected from the variation of PZC with Al/(Al + Si) found with the synthetic aluminosilicates (Figure 3).

A slight negative adsorption of Na^+ or Cl^- was observed with some samples (Figures 1 and 2). This apparent negative adsorption was not considered because the experimental method used assumes that all of the water lost on drying at 105°C contained NaCl at the same concentration as the bulk solution and this may not have been so (Schofield, 1949).

DISCUSSION

Hydrous oxides

The results obtained with hydrous silica are similar to those reported by other workers using cation exchange (Houng *et al.*, 1966; Strazhenko *et al.*, 1974) and potentiometric titration (Bolt, 1957) methods. The pH-dependent negative charge present arises from ionization of the weakly acidic surface silanol groups (Si—OH ⇌ Si—O^- + H^+).

The presence of only pH-dependent positive charge on the hydrous alumina is also consistent with results obtained by Houng *et al.* (1966). This charge arises from protonation of the hydrous oxide surface on the acid side of the point of zero charge (Jackson, 1963) (Al—OH + H^+ ⇌ Al—OH_2^+). No negative charges would be expected when the pH of the suspension is less than the zero point of charge, which is 9.3 for this sample (Rajan *et al.*, 1974).

Synthetic aluminosilicates

The structural models for amorphous aluminosilicates proposed by Cloos *et al.* (1969) and van Reeuwijk and de Villiers (1970) provide a useful basis for understanding the surface charge characteristics of these materials. These models consider amorphous aluminosilicates to be composed of two intimately associated phases: an aluminosilicate phase resulting

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from the isomorphous substitution of tetrahedrally co-ordinated Al for Si in a silica structure with a negative charge which is neutralized, at least partially, by a positively charged phase composed of hydroxy-aluminium species. At low values of the Al/(Al + Si) ratio, the charge balancing hydroxy-aluminium species are thought to be monomeric or simple polymeric cations. These species become more polymeric as the Al/(Al + Si) ratio increases (Cloos *et al.*, 1969).

The pH-dependent positive charges observed with the amorphous aluminosilicates will arise by protonation of the charge-balancing hydroxy-aluminium species, as shown above for the hydrous aluminium oxide. Although no positive charge was detected in sample A [Al/(Al + Si) = 0.29], this does not necessarily indicate that there were no charge-balancing hydroxy-aluminium species in this sample. Sumner (1963) pointed out that where conditions enable the double layers surrounding positive and negative charges in soils to overlap, mutual neutralization occurs, preventing retention of counter-ions at these sites. The average distance between negative and positive charges would be smaller (and the degree of double layer overlap therefore greater) in sample A than in the other aluminosilicates because of the relatively small size of any charge-balancing hydroxy-aluminium species. Interaction between these close oppositely charged sites could have prevented the detection of positive charge in sample A by the methods used (Fey and le Roux, 1976), whereas, in the other aluminosilicates, only those positive charges on the larger hydroxy-aluminium species which are closest to the negative charges would be masked.

The negative charge below about pH 6 can be attributed to the isomorphous substitution of tetrahedral Al in the silicate structure. By analogy with the crystalline layer clay minerals, the resulting negatively charged sites would be expected to be strongly acidic. The pH-dependence of the negative charge in this pH range probably arises from the release of initially blocked permanent negative charge by protonation of the charge-balancing hydroxy-aluminium species (de Villiers and Jackson, 1967). However, it is possible that the negatively charged sites have an acidic character of medium strength and therefore exhibit pH-dependence in this range. As no negative charge was detected below pH 6 in samples D [Al/(Al + Si) = 0.64] and E [Al/(Al + Si) = 0.87], any negative charge due to isomorphous substitution must be completely blocked by charge-balancing material in these samples.

Extra negative charge developed at pH values above 6 will, as in silica, be due to ionization of silanol groups. The silanol groups involved may be present as silicate absorbed on the hydroxy-aluminium material as well as structural silicate (Rajan and Perrott, 1975; Rajan, 1975). The development of negative charge in alkaline conditions was attributed by Fey and le Roux (1976) solely to charge reversal of edge Al—OH_2 functional groups in the polymeric hydroxy-aluminium material. However, the relatively high PZC of pure amorphous aluminium hydroxide (Parks, 1965) indicates that charge reversal at these groups would not make a contribution to the negative charge at pH values less than about 8.

Soil clays

It is likely that the sources of surface charge discussed for the synthetic aluminosilicates will also be operating with soil allophanes. However, in addition, hydrous iron (III) oxides, present either as a separate phase or as hydroxy-iron species adsorbed at cation exchange sites, would be expected to provide positive charges at low pH. The hydrous iron (III) oxide may also contribute to the negative charge at high pH values if its own point of zero charge is low enough (Greenland, 1975).

CONCLUSIONS

Amorphous aluminium hydroxide is unstable, aging to crystalline forms such as bayerite or gibbsite depending on conditions. However, aging can be prevented or retarded by the presence of anions (Nail *et al.*, 1976) or negatively charged surfaces (de Villiers, 1969). In many soils, negatively charged crystalline clay minerals and organic or inorganic anions are thought to stabilize hydroxy-aluminium, and possibly also hydroxy-iron species (de Villiers, 1969). Current structural models for soil allophane envisage stabilization of a highly reactive hydroxy-aluminium phase by interaction with negative charges resulting from isomorphous substitution in an aluminosilicate 'core'.

Besides providing sites for retention of specifically adsorbed anions like phosphate (Perrott *et al.*, 1974), hydroxy-aluminium and hydroxy-iron species play an important role in determining surface charge. These species are a source of pH-dependent positive charge and appear to cause the pH-dependence of negative charge by variation in the blocking of permanent negative charge with pH. Deprotonation of silanol groups in structural or adsorbed silicate provides another source of pH-dependent negative charge at high pH values.

Although similarity between the surface charge characteristics of synthetic amorphous aluminosilicates and soil allophanic clay has been demonstrated, the presence of specifically adsorbed organic and inorganic anions has an important effect. The results of an investigation into their influence will be the subject of a separate report.

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