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## Surface charge characteristics of kaolinitic tropical soils

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**Abstract**—Surface charge properties of four representative kaolinitic soils from the humid tropics (Brazil) were investigated by a methodology involving independent measurements of net total permanent and variable charge components. Permanent structural charge was determined by Cs<sup>+</sup> adsorption, whereas variable charge was quantified by simultaneous proton titration and background electrolyte (LiCl) adsorption measurements. Data were obtained for homoionic soils suspended in LiCl solutions of ionic strength 1–10 mmol L<sup>-1</sup> and pH value 2–6. Corrections were made in the titration data for proton consumption resulting from dissolution and aqueous-phase complexation reactions. Conjunctive use of proton titration and electrolyte adsorption data yielded independent assessments of proton surface charge densities and points of zero charge. The surface charge data were tested successfully for consistency with the law of surface charge balance.

Three of the soils exhibited similar surface charge behavior, with no pronounced effect of differences in either organic C or Fe and aluminum oxide content. One soil containing significant manganese oxides showed points of zero charge well below those of the other three soils. The point of zero net charge (p.z.n.c.) for the soils was  $\leq 4$ , lower than values reported for specimen kaolinite. The point of zero net proton charge (p.z.n.p.c.) increased with decreasing ionic strength. In all cases, the presence of small quantities of structural charge in 2:1 clay minerals had a significant effect on surface charge properties; e.g., for all soils, p.z.n.c. < p.z.n.p.c. These characteristics of surface charge were shown to be consistent with the behavior of a mixture of kaolinite, organic matter, and a small quantity of 2:1 clay minerals. In conformity with the law of surface charge balance, ionic strength effects were found to be removed by plotting net adsorbed ion charge against net proton surface charge density.

### INTRODUCTION

Soils of the humid tropics play an essential role in global erosion and geochemical cycling processes. They contribute about half of the total river solid load to the oceans (Stallard, 1988) and have come to prominence as critical mediators of the global cycles of carbon, nitrogen, and other chemical elements because of rapidly-changing land-use practices in the tropical Americas (Crutzen and Andreae, 1990). A process-based understanding of this role, however, is lacking because detailed information about the principal chemical reactions involved is not available (Stewart et al., 1990). The short-term chemical mediation of erodibility and geochemical cycles in soil is principally by surface reactions on soil particles (Sposito, 1989a). Both minerals and organic matter come into these reactions, which have long been a challenging area of research because of the complexity of the organic matter and the difficulty of developing laboratory methodologies that respect the structural fragility and the unique surface chemical properties of the mineral mixtures in these soils (Theng, 1980).

### Surface Charge Balance

The surface charge of soil particles affects their adsorption, dissolution, and colloidal reactions and, therefore, influences the transport and fate of solutes, rates of chemical weathering,

and erodibility at the land surface. Measurements of surface charge for soil particles must account explicitly for the diversity and conditional nature of the four principal components that contribute to this quantity.

Irrespective of soil provenance, solid particle surfaces in soils develop electrical charge because of permanent, isomorphous substitutions between ions of differing valence within soil mineral structures and because of reactions of surface functional groups with adsorptive species in solution (Sposito, 1989a). Four components of surface charge contribute to the net total particle surface-charge density,  $\sigma_p$ . The net permanent structural surface-charge density,  $\sigma_o$ , is created by isomorphous substitutions in soil minerals. These substitutions occur in both primary and secondary minerals, but they produce significant (negative) surface charge only in the 2:1 layer-type aluminosilicates (Dixon and Weed, 1989). The net proton surface-charge density,  $\sigma_H$ , is created by differences between the moles of protons and the moles of hydroxide ions complexed by surface functional groups. The net inner-sphere complex surface-charge density,  $\sigma_{IS}$ , results from the net total charge of ions, other than H<sup>+</sup> and OH<sup>-</sup>, which are bound into inner-sphere surface coordination. The net outer-sphere complex surface-charge density,  $\sigma_{OS}$ , results from the net total charge of ions, other than H<sup>+</sup> and OH<sup>-</sup>, which are bound into outer-sphere surface coordination. The net total particle surface charge,  $\sigma_p$ , is the sum of these four components (Sposito, 1989a):

$$\sigma_p = \sigma_o + \sigma_H + \sigma_{IS} + \sigma_{OS}. \quad (1)$$

If  $\sigma_p$  is non-zero, it must be balanced by the diffuse layer

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surface-charge density,  $\sigma_D$ , which is equal in magnitude, but opposite in sign to  $\sigma_P$ . The law of surface charge balance may then be written

$$\sigma_P = -\sigma_D. \quad (2)$$

Ions contributing to  $\sigma_D$  are distinguished from those contributing to  $\sigma_{IS}$  or  $\sigma_{OS}$  by their more extensive solvation and shorter residence time (ca. 10 ps) as adsorbed species (Sposito, 1992). For complex adsorbents, including tropical soils, surface charge is likely to be distributed unequally among the many solid phases present because of differences in structural charge, surface site density, and specific surface area. For these systems, surface charge components in Eqns. 1 and 2 can be least ambiguously measured on a mass basis and expressed as specific surface charge, in S.I. units of moles of charge per kilogram ( $\text{mol}_e \text{ kg}^{-1}$ ).

The right side of Eqn. 1 indicates the contributions of both permanent ( $\sigma_O$ ) and conditional ( $\sigma_H$ ,  $\sigma_{IS}$ ,  $\sigma_{OS}$ ) components to particle surface charge. The value of  $\sigma_O$  is dependent only upon the composition and structure of solid phases while the values of the remaining components depend upon the nature of both the solid and solution phases. In general, temperate-zone soils, containing large quantities of 2:1 layer-type clay minerals, have been modeled as permanent-charge systems (Bolt, 1982), whereas the highly weathered soils of the humid tropics, comprising predominantly kaolinite, iron, and aluminum oxides, and quartz, have been modeled as conditional-charge systems (van Raij and Peech, 1972; Juo, 1981; Singh and Uehara, 1986). These distinctions are idealizations; but the assumptions they invoke are often reflected in the interpretation of experimental data.

### Points of Zero Charge

The net adsorbed ion charge is given by

$$(q_+ - q_-) = \sigma_{IS} + \sigma_{OS} + \sigma_D, \quad (3)$$

where  $q$  refers to adsorbed cation (+) or anion (-) charge irrespective of surface speciation (Sposito, 1989a). The point of zero net charge (p.z.n.c.) is defined as the pH value where the left side of Eqn. 3 ( $\Delta q$ ) is equal to zero. Substitution of the left side of Eqn. 3 into Eqns. 1 and 2 provides a means to assess experimentally the intrinsic surface charge density (Sposito, 1989a):

$$\sigma_m \equiv \sigma_O + \sigma_H = -(q_+ - q_-). \quad (4)$$

The point of zero net proton charge (p.z.n.p.c.) is defined as the pH value where  $\sigma_H = 0$ ; by Eqn. 4, this is also the pH value where  $\sigma_O = -\Delta q$ .

For titrations of single oxide minerals suspended in indifferent background electrolyte solutions (electrolyte ions that do not interact chemically with a surface, but only by coulombic forces), the most common procedure to estimate the p.z.n.p.c. is to equate it with the pH value at the common intersection point of titration curves obtained at different ionic strengths (van Leeuwen and Lyklema, 1986). This intersection point was termed the point of zero salt effect (p.z.s.e.) by Parker et al. (1979). However, model calculations indicate that a p.z.s.e. is not expected, a priori, for arbitrary solid phase mixtures, even in the absence of specific ion adsorption (Bolt

and van Riemsdijk, 1987). This prediction is supported by data from titrations performed on complex mixtures (e.g., Parker et al., 1979; Hendershot and Lavkulich, 1983), suggesting that equating of the p.z.n.p.c. to the p.z.s.e. is not feasible for these mixtures. Direct measurement of the p.z.n.p.c. for soils and other heterogeneous mixtures (Charlet and Sposito, 1987; Anderson and Sposito, 1992) can reduce ambiguity associated with the determination of net proton surface charge density.

### Surface Charge in Tropical Soils

Conceptual models have been developed to describe quantitatively the surface charge components in Eqns. 1 and 2, the points of zero charge, and the distribution of ions at solid particle surfaces (James et al., 1975; van Olphen, 1977; Sposito, 1984; Davis and Kent, 1990; Goldberg, 1992). Evaluation of these models for the surface chemistry of natural soil systems has taken place over the past 20 years (e.g., van Raij and Peech, 1972; Parker et al., 1979; Gillman and Uehara, 1980; Uehara and Gillman, 1980; Theng, 1980; Charlet and Sposito, 1987, 1989; Goldberg, 1992; Duquette and Hendershot, 1993). A major driving force for this application has been the growing interest in the aqueous geochemistry of highly weathered, tropical soils comprising a complex mixture of amphoteric solid inorganic and organic surfaces. The acid-base chemistry of these soils is quite variable: when in contact with indifferent electrolyte solution at the pH values commonly encountered in acidic tropical soils (pH 3–6), the variable-charge sites of a given solid constituent may be net uncharged, net positively charged, or net negatively charged. Previous work has shown that the relative content of mineralogical and organic soil constituents can greatly affect the surface chemical properties of kaolinitic tropical soils (e.g., Parfitt, 1981; Juo, 1981; Marcano-Martinez and McBride, 1989). The variable-charge behavior of the bulk soil will reflect the contributions of these diverse constituents; however, soil mineral constituents may differ in surface behavior from their geological or synthetic counterparts. For example, Singh and Gilkes (1992) studied chemical and physical properties of soil kaolinites from Australia and found that the soil kaolinites were structurally disordered and irregular, contained appreciable quantities of Fe in their structures, and had larger surface areas and  $\Delta q$  values than a specimen Georgia kaolinite. They concluded that data obtained on mineral specimens might not be relevant to soil kaolinites, although single component systems do provide a reference necessary to ascertaining the solid constituents that control the surface chemistry of complex soil adsorbents.

The objectives of the present work were (1) to evaluate experimentally the surface charge components of kaolinitic soils from the tropics, comprising variable quantities of mineral and organic constituents; (2) to test the proposed equality between p.z.s.e. and p.z.n.p.c.; and (3) to compare the surface charge behavior of the soils to that reported previously for their constituent solid phases.

## MATERIALS AND METHODS

### Soil Samples

Samples of the surface horizons of four kaolinitic soils in isothermic regions of Brazil were provided by Dr. Cheryl Palm (Nat-

ural Resource Ecology Laboratory, Colorado State University) for use in the present study. Soil samples MF and MC were collected 50 km outside of Manaus (Amazonas state) from sites in moist tropical rainforest or cultivated ecosystems, respectively. Soil sample OP, collected near Ouro Preto (Rondonia state), and soil sample UNA, collected near Arataca (Bahia state), were both obtained in moist tropical rainforest. Details of the soil sampling procedures and chemical and physical data pertaining to the soils are described by Motavalli et al. (1994, 1995). X-ray diffraction, differential thermal and chemical analyses indicate that the solid phase in the soils is dominated by kaolinite, with variable smaller quantities of Fe and Al oxides, 2:1 clay minerals, organic matter, and quartz. A summary is presented in Table 1.

### Permanent Surface Charge Density

Cesium-accessible structural charge was measured by a modification of the method of Anderson and Sposito (1991). Full details of the modified method are given by Chorover and Sposito (1993). Briefly, field-moist soil samples were reacted repeatedly with CsCl to prepare a Cs-saturated adsorbent free of entrained electrolyte, then heated at 65°C for 48 hr to enhance the formation of inner-sphere Cs<sup>+</sup> surface complexes with 2:1 clay minerals. The dried adsorbent was subsequently reacted with LiCl at pH 6 to displace Cs<sup>+</sup> from weaker adsorption sites. The Cs<sup>+</sup> retained against Li<sup>+</sup> exchange was extracted with ammonium acetate to provide an estimate of  $\sigma_0$ .

### Net Proton and Adsorbed Ion Surface Charge Densities

A discontinuous titration procedure was used to measure proton and background electrolyte adsorption (Charlet and Sposito, 1987). Relative changes in  $\sigma_H$  were calculated after corrections were made for proton consumption and/or yield resulting from dissolution and aqueous-phase complexation reactions. These relative changes are converted into absolute values of  $\sigma_H$  after the p.z.n.p.c. is established (Sposito, 1992).

A soil sample first was reacted with LiCl, a 1-1 background electrolyte with easily replaceable cation and anion, to facilitate the simultaneous measurement of index ion surface charge in the discontinuous titration experiments. Approximately 0.035 kg of field moist soil was transferred into 250 ml polycarbonate centrifuge bottles. The sample was suspended in 0.2 kg of 0.5 mol kg<sup>-1</sup> LiCl adjusted to pH 5.5 with LiOH and mixed by gentle rotation at 7 rpm for 1 hr. The

suspension was then removed from the mixer and allowed to settle for 15 min. Forceps were used to remove light-fraction organic matter from the suspension surface. The suspension was centrifuged at 13,000 relative centrifugal force (RCF) for 15 min. The supernatant solution was aspirated via Pasteur pipette into a filter flask and discarded. The sample was resuspended in 0.5 mol kg<sup>-1</sup> LiCl at pH 5.5 and the treatment repeated. The sample was then resuspended in 0.2 kg of 0.1 mol kg<sup>-1</sup> LiCl, mixed by rotation for 30 min, and centrifuged at 13,000 RCF for 15 min. Following aspiration of the supernatant solution, reaction of the sample with 0.1 mol kg<sup>-1</sup> LiCl was repeated. The sample was finally reacted once with 0.2 kg of 0.01 mol kg<sup>-1</sup> LiCl adjusted to pH 4.1 with 0.01 mol kg<sup>-1</sup> HCl, mixed by rotation for 30 min, and centrifuged at 13,000 RCF for 30 min.

Following aspiration of the supernatant solution, the sample was transferred to sterile polystyrene petri dishes and mixed to produce a uniform soil paste. Triplicate 500 mg subsamples of each paste were transferred to acid-washed oven-dried, ceramic crucibles. The paste samples were then oven-dried to constant mass at 110°C to determine water content. The remaining pastes were stored in sealed polystyrene containers at 4°C until use.

In each proton titration experiment, the output from the pH electrode was calibrated in terms of H<sup>+</sup> concentration, instead of H<sup>+</sup> activity as used by Charlet and Sposito (1987) and Anderson and Sposito (1992), in order to avoid a need for activity-coefficient models. The standard electrode potential,  $E'_0$ , was determined by Gran titration (Gran, 1952; Pehrsson et al., 1976; Chorover and Sposito, 1993) in the same ionic media as used in a given titration experiment. Standardized HCl was titrated by ten stepwise additions of standardized LiOH on the acid side of the equivalence point (EP). The volume of titrant added at the EP ( $V_e$ ), was determined by linear regression. A value of  $E'_0$  was then calculated for each point in the titration and the mean value was used for subsequent determinations of  $-\log [H^+]$ . Error in assessment of  $E'_0$ , arising primarily from uncertainty in calculation of  $V_e$ , was consistently less than 0.4 mV. The calibration was checked against reference standards following measurements of sample proton concentrations. An Orion-Ross model 8102 glass combination electrode was used with a Beckman  $\Phi$  71 pH meter reading in emf for the measurement of H<sup>+</sup> concentration. All stock solutions and dilutions were prepared using distilled water that had been passed through a Milli-Q<sup>®</sup> water purification unit.

All batch reaction systems, corresponding to a given soil sample, ionic strength ( $I$ ), and  $-\log [H^+]$ , were prepared in duplicate. A measured mass of soil paste containing approximately 350 mg of dry

TABLE 1. Selected physical and chemical data pertaining to the four kaolinitic soils (Motavalli et al., 1994, 1995). Standard deviations are given in parentheses.

Soil	Depth (cm)	Particle Size				Org-C <sup>1</sup> (g kg <sup>-1</sup> )	Fe <sub>DCB</sub> <sup>2</sup>	Fe <sub>OX</sub> <sup>3</sup>	Surface Area <sup>4</sup> (m <sup>2</sup> g <sup>-1</sup> )	$\sigma_0$ <sup>5</sup> (mmol <sub>c</sub> kg <sup>-1</sup> )	Clay Mineralogy <sup>6</sup>
		Sand	Silt	Clay							
MF	0-8	234(9)	10(6)	750(17)	33(3)	15.5(0.17)	1.76(0.02)	64(5.7)	-19(1)	K,v	
MC	0-20	218(5)	36(8)	750(10)	17(3)	N.A. <sup>7</sup>	N.A.	N.A.	-12.5(0.4)	K,v	
OP	0-12	673(6)	180(8)	150(10)	12(2)	126(1.4)	5.2(0.16)	104(5)	-8.3(0.6)	K,v,hiv,go	
UNA	0-12	71(14)	580(30)	83(1.4)	32(5)	200(2.4)	1.89(0.02)	83(1.4)	-15(2)	K,GO,gi,hiv	

<sup>1</sup>Organic carbon measured by CHN analyzer

<sup>2</sup>Citrate-dithionite-bicarbonate extractable iron (Jackson et al., 1986)

<sup>3</sup>Acid-ammonium-oxalate extractable iron (Jackson et al., 1986)

<sup>4</sup>Measured by ethylene-glycol-monoethyl ether adsorption (Heilman et al., 1965) for clay fraction only.

<sup>5</sup>Cesium-accessible permanent surface charge density, determined in the present study.

<sup>6</sup>Mineralogical composition of the < 2  $\mu$ m fraction as determined by x-ray diffraction and differential thermal analysis. Upper case letters indicate major components, lower case letters indicate minor components: k = kaolinite, v = vermiculite, hiv = hydroxy-interlayer vermiculite, go = goethite, gi = gibbsite.

<sup>7</sup>Data not available.

soil was added to weighed, acid-washed 35 ml polyallomer centrifuge tubes. The sample was suspended in 0.035 kg of LiCl/HCl or LiCl/LiOH solution at  $I = 0.001, 0.005$  or  $0.01 \text{ mol kg}^{-1}$ . Mixtures of electrolyte, acid, and base solutions of equivalent ionic strength were prepared to reach equilibrium supernatant solution  $-\log [\text{H}^+]$  values between 2 and 6. Immediately following preparation of the corresponding soil suspension, blank solution mixtures (no soil added), were prepared in duplicate by addition of electrolyte, acid, and base solutions in exactly the same proportions as those used for the soil suspension.

The suspensions and blanks were reacted at  $25^\circ \pm 2^\circ\text{C}$  in a temperature-controlled laboratory for 3 hr with gentle rotation at 7 rpm. The 3 hr reaction time was chosen to permit sufficient equilibration ( $[\text{H}^+]$  stabilized after 0.3 hr) while minimizing particle alteration and back-reactions between solid and solution resulting from solid phase dissolution. The suspensions were then centrifuged at 27,000 RCF and  $25^\circ \pm 1^\circ\text{C}$  for 20 min. The supernatant solution was carefully aspirated by Pasteur pipette into an acid-washed, 60 ml high density polyethylene (HDPE) container and a subsample was taken for immediate measurement of emf calibrated to  $-\log [\text{H}^+]$ . Measurement of  $-\log [\text{H}^+]$  for a blank followed that of the corresponding supernatant solution. Electrode/solution equilibration was considered complete after 5–10 min, when emf changed by less than  $0.1 \text{ mV min}^{-1}$ . The remaining supernatant solution in the HDPE container was acidified to pH 2 by addition of  $\text{HNO}_3$  and stored at  $4^\circ\text{C}$  prior to chemical analysis.

The polyallomer tubes containing the soil samples and entrained solutions were weighed and the mass of entrained solution was determined. The samples were then reacted with  $0.03 \text{ kg}$  of  $1.0 \text{ mol kg}^{-1} \text{NH}_4\text{NO}_3$  solution for 30 min at low speed on a reciprocal shaker and centrifuged for 10 min at 27,000 RCF. The supernatant solution was aspirated by Pasteur pipette into an acid-washed, pre-weighed 60 ml HDPE container. The  $\text{NH}_4\text{NO}_3$  exchange step was repeated. Both extraction solutions were quantitatively combined and the total mass of solution was recorded. This solution was acidified to pH 2 by addition of  $\text{HNO}_3$  and stored at  $4^\circ\text{C}$  prior to chemical analysis.

### Chemical Analyses

The concentration of  $\text{Cs}^+$  in the LiCl and ammonium acetate extracts was determined by atomic emission spectroscopy, with calibration standards prepared on a mass basis in the same electrolyte matrices as the samples. All dilutions were made on a mass basis with the matrix solutions.

The concentration of index cation,  $\text{Li}^+$ , and the background metals, (Ca, Mg, Mn, and Al) in the LiCl supernatant solution and the  $\text{NH}_4\text{NO}_3$  extractant were measured by inductively-coupled plasma atomic emission spectroscopy (ICPAES). All sample solution  $\text{Li}^+$  concentrations exceeded the detection limit of  $0.5 \text{ mg kg}^{-1}$ . The detection limits for Al, Ca, Mg, and Mn were 23, 0.2, 0.15, and  $1.6 \mu\text{g kg}^{-1}$ , respectively. The concentrations of  $\text{Na}^+$  and  $\text{K}^+$  in both supernatant solutions and extracting solutions were found to be negligible by atomic absorption spectroscopy. Calibration standards were prepared on a mass basis from ICPAES reference standards (AMEX Inc.) in the LiCl and  $\text{NH}_4\text{NO}_3$  matrices used in the discontinuous titration experiments.

The concentration of index anion,  $\text{Cl}^-$ , in the LiCl supernatant solution and the  $\text{NH}_4\text{NO}_3$  extract solution were measured by  $\text{Ag}^+$  titration using a Buchler digital chloridometer. The combination of low  $\text{Cl}^-$  and high salt concentrations in the  $\text{NH}_4\text{NO}_3$  extracts increased detection limits from  $<0.05$  to  $0.4 \text{ mmol kg}^{-1}$  and necessitated the use of a modified standard addition method for  $\text{Cl}^-$  analysis in these samples (Harris, 1987). Small concentrations of  $\text{Cl}^-$  in high salt matrices were measured accurately in the presence of an added  $\text{Cl}^-$  concentration of  $0.70 \text{ mmol kg}^{-1}$ .

### Data Analyses

Accessible structural surface charge was calculated as the surface excess of  $\text{Cs}^+$  retained following  $\text{Cs} \rightarrow \text{Li}$  exchange (Anderson and Sposito, 1991):

$$-\sigma_0 = N_{\text{Cs, tot}(\text{NH}_4\text{C}_2\text{H}_3\text{O}_2)} - M_{\text{entr}} m_{\text{Cs}(\text{LiCl})} \quad (5)$$

where  $N_{\text{Cs, tot}(\text{NH}_4\text{C}_2\text{H}_3\text{O}_2)}$  is the total number of moles of  $\text{Cs}^+$  per unit adsorbent mass collected in the ammonium acetate extraction step,  $m_{\text{Cs}(\text{LiCl})}$  is the molinity (moles per kilogram of solution) of  $\text{Cs}^+$  in the LiCl supernatant solution per unit adsorbent mass, and  $M_{\text{entr}}$  is the mass of entrained LiCl solution.

The surface excess,  $q_i$ , of ion  $i$ , in moles of charge per kilogram of dry adsorbent, following a 3 hr equilibration period was calculated from (Sposito, 1989a)

$$q_i = |z_i| n_{i,(\text{NH}_4\text{NO}_3)} - M_{\text{entr}} |z_i| m_i \quad (6)$$

where  $z_i$  is the valence of ion  $i$ ,  $n_{i,(\text{NH}_4\text{NO}_3)}$  is the number of moles of ion  $i$  per unit dry adsorbent mass extracted in the  $\text{NH}_4\text{NO}_3$  step,  $M_{\text{entr}}$  is the mass of entrained LiCl solution per unit dry adsorbent mass, and  $m_i$  is the molinity of species  $i$  in the supernatant solution. Surface excesses were calculated for  $\text{Li}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$ .

The apparent proton surface charge density,  $\sigma_{\text{H, titr}}$ , was calculated for each  $-\log [\text{H}^+]$  and  $I$  from the difference between the final  $\text{H}^+$  and  $\text{OH}^-$  concentrations of a sample and those of a blank:

$$\sigma_{\text{H, titr}} = M_{\text{soln}} \left\{ ([\text{H}^+]_b - [\text{H}^+]_s) - \left( \frac{K_{\text{wc}}}{[\text{H}^+]_b} - \frac{K_{\text{wc}}}{[\text{H}^+]_s} \right) \right\} \quad (7)$$

where  $M_{\text{soln}}$  is the mass of electrolyte solution equilibrated with the soil per unit adsorbent mass,  $[\text{H}^+]$  is the solution proton concentration (moles  $\text{kg}^{-1}$ ),  $K_{\text{wc}} = 10^{-14} \text{ mol}^2 \text{ kg}^{-2}$  is a conditional dissociation product of water, and the subscripts s and b refer to sample and blank, respectively.

In the acid range of the titrations ( $\text{pH} < 4.5$ ), soluble Al was observed to increase significantly with increasing proton concentration, evidently from mineral dissolution. Titration measurements were corrected in this pH range by assuming that Al was released as the species  $\text{Al}^{3+}$  (Nordstrom and May, 1989). Thus, Eqn. 7 was rewritten to account for Al dissolution:

$$\sigma_{\text{H, titr}} = M_{\text{soln}} \left\{ ([\text{H}^+]_b - [\text{H}^+]_s) - \left( \frac{K_{\text{wc}}}{[\text{H}^+]_b} - \frac{K_{\text{wc}}}{[\text{H}^+]_s} \right) - 3[\text{Al}]_s \right\} \quad (8)$$

where  $[\text{Al}]_s$  is the observed soluble Al in a given titration experiment. Equation 8 was applied only to that part of a titration exhibiting proton-promoted Al dissolution behavior. At  $\text{pH} > 5$ , the speciation of Al in the presence of soluble organic compounds is problematic because of the potential for soluble complex formation; even the assumption of inorganic monomeric Al is not routinely verifiable at low pH (Luster et al., 1993).

The net proton surface charge density,  $\sigma_{\text{H}}$ , for a given  $-\log [\text{H}^+]$  and  $I$ , is defined as the difference between the apparent proton surface charge density at that  $-\log [\text{H}^+]$  and the apparent proton surface-charge density at the p.z.n.p.c. (Charlet and Sposito, 1987):

$$\sigma_{\text{H}}(-\log [\text{H}^+], I) \equiv \sigma_{\text{H, titr}} - \sigma_{\text{H, titr}}(\text{p.z.n.p.c.}, I) \quad (9)$$

From Eqn. 4,

$$\sigma_{\text{H}}(-\log [\text{H}^+], I) = -\{(q_+ - q_-) + \sigma_0\} \quad (10)$$

and, therefore (Anderson and Sposito, 1992),

$$\sigma_{\text{H, titr}}(\text{p.z.n.p.c.}, I) = \sigma_{\text{H, titr}}(-\log [\text{H}^+], I) + \sigma_0 + (q_+ - q_-) \quad (11)$$

A value for the right side of Eqn. 11 was calculated for each titration point at a given ionic strength. An average value of  $\sigma_{\text{H, titr}}(\text{p.z.n.p.c.}, I)$  was taken as the mean of these values.

The p.z.n.c. at each ionic strength was calculated by fitting net ion adsorption data (Eqn. 6) to a second-order polynomial function of  $-\log [\text{H}^+]$  by quadratic regression and solving for  $-\log [\text{H}^+]$  in the resultant function at the condition  $\Delta q = (q_+ - q_-) = 0$ . Although the surface excess of  $\text{Li}^+$  dominated the value of adsorbed cation charge, pH-dependent adsorption of smaller quantities of bivalent ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$ ) was observed (Chorover, 1993)

and was included in the calculation of the net adsorbed ion charge density,  $\Delta q$ .

The p.z.n.p.c. for each soil was calculated in two ways (cf. Anderson and Sposito, (1992)): (1) the complete  $\sigma_H$  dataset was fit to a second-order polynomial function of  $-\log [H^+]$  by quadratic regression and the resultant function was solved for  $-\log [H^+]$  at the condition  $\sigma_H = 0$  (Eqn. 9); (2) the complete net ion adsorption dataset ( $\Delta q$ ) was fit to a second-order polynomial function of  $-\log [H^+]$  by quadratic regression and the resultant function was solved for  $-\log [H^+]$  at the condition  $\Delta q = -\sigma_O$  (Eqn. 4). Comparison of the p.z.n.p.c. values calculated in these two ways provides a test of the mutual consistency of the titration and ion-adsorption data (Anderson and Sposito, 1992).

## RESULTS

### Permanent Charge

Values of the permanent charge density,  $\sigma_O$ , as measured by the  $Cs^+$  adsorption method are listed for the four soils in Table 1. As is typical for highly-weathered soils, the observed magnitudes of  $\sigma_O$  are very small in absolute value and would require a soil content of only about  $10 \text{ g kg}^{-1}$  vermiculite to produce. [The value of  $|\sigma_O|$  for specimen vermiculite is  $1200\text{--}1500 \text{ mmol}_c \text{ kg}^{-1}$  (Sposito, 1984)]. This content of vermiculite is barely detectable by X-ray diffraction (XRD) techniques, attesting to the high sensitivity of the method. Anderson and Sposito (1991) measured a  $|\sigma_O|$  value of just  $0.33 \text{ mmol}_c \text{ kg}^{-1}$  for a Brazilian surface soil whose XRD patterns had indicated that 2:1 layer-type clay minerals were undetectable.

### Adsorbed Ion Charge

Net adsorbed ion charge ( $\Delta q$ ) data for each soil sample at each ionic strength are presented in Fig. 1. Complete tabulation of these data and the individual components of  $\Delta q$  appears in Chorover (1993). The adsorbed cation charge ( $\Sigma q_+$ ) includes contributions of the index cation,  $Li^+$ , and the bivalent cations,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Mn^{2+}$ . The magnitude of  $\Sigma q_+$  increased with pH and I for the Manaus (MF and MC) and Una (UNA) soils. Ionic strength effects were less evident for the Ouro Preto (OP) soil, which contained higher sand content, although the trend in pH remained. The values of  $q_{Ca^{2+}}$  and  $q_{Mn^{2+}}$  were largest for soil OP and accounted for approximately half of  $\Sigma q_+$  at a given pH and ionic strength. The magnitude of  $q_{Cl^-}$  decreased with increasing pH, but its pH and ionic strength dependencies were small relative to those of  $q_{Li^+}$ . Net adsorbed ion charge increased with increasing ionic strength at pH values above the intersections of the  $\Delta q$  curve for the MF, MC, and UNA soils. The pH values where the quadratic regressions of  $\Delta q$  on  $-\log [H^+]$  (solid, dashed, and dotted lines in Fig. 1) are equal to zero defines an experimentally determined p.z.n.c. The p.z.n.c. values for the soils (Table 2) were essentially independent of background electrolyte concentration, since pH when  $\Delta q = 0$  coincided with the pH values where the quadratic  $\Delta q$  regression curves converged.

### Proton Surface Charge

Net proton surface charge densities,  $\sigma_H$ , calculated from Eqn. 9, are presented in Fig. 2. Complete tabulation of these data and  $\sigma_{H,itr}$  (p.z.n.p.c.) values appears in Chorover (1993).

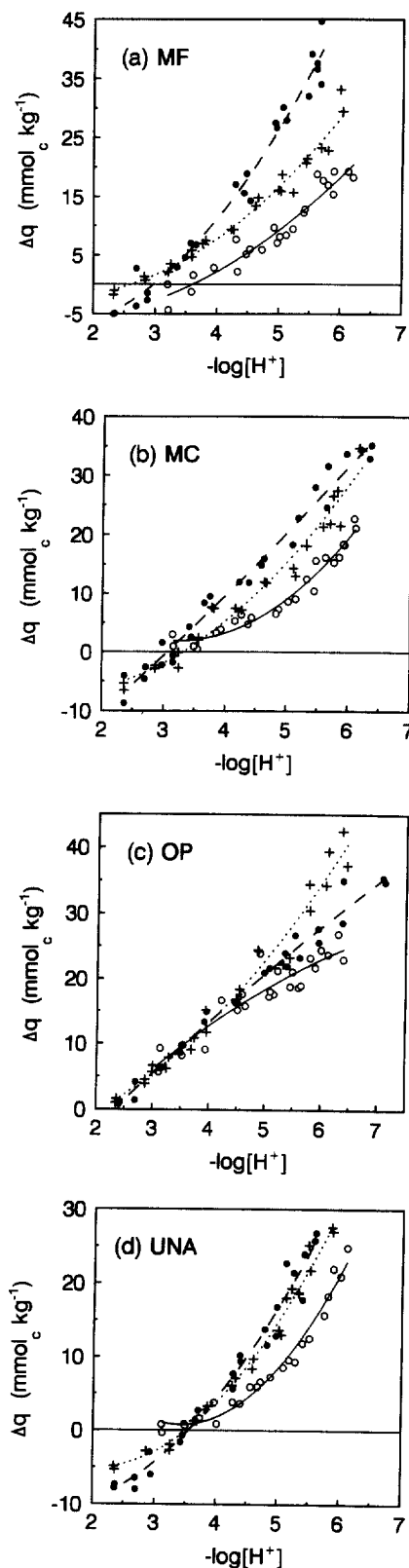


FIG. 1. Net adsorbed ion charge density ( $\Delta q$ ) vs. pH: (a) MF, (b) MC, (c) OP, (d) UNA. Adsorbed cation charge ( $q_+$ ) includes contributions from  $Li^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Mn^{2+}$ . Ionic strength: open circles- $0.001 \text{ mol kg}^{-1}$ ; crosses- $0.005 \text{ mol kg}^{-1}$ ; filled circles- $0.01 \text{ mol kg}^{-1}$ . Solid, dotted and dashed lines are quadratic regression results for the data at  $0.001$ ,  $0.005$  and  $0.01 \text{ mol kg}^{-1}$ , respectively.

TABLE 2. Points of zero net charge (p.z.n.c.) and points of zero net proton charge (p.z.n.p.c.) for three ionic strengths (LiCl). Standard deviations are given in parentheses.

Soil	p.z.n.c.	p.z.n.p.c. <sup>1</sup>	p.z.n.p.c. <sup>2</sup>
		0.001 mol kg <sup>-1</sup>	
MF	3.6 (0.3) <sup>3</sup>	6.1 (0.3) <sup>4</sup>	6.0 (0.2) <sup>5</sup>
MC	< 3.1 <sup>6</sup>	5.3 (0.4)	5.4 (0.3)
OP	< 3.0 <sup>6</sup>	3.5 (0.5)	3.4 (0.4)
UNA	< 3.1 <sup>6</sup>	5.7 (0.4)	5.6 (0.3)
		0.005 mol kg <sup>-1</sup>	
MF	2.6 (0.3)	5.2 (0.2)	5.2 (0.2)
MC	3.3 (0.3)	4.7 (0.4)	4.7 (0.2)
OP	2.2 (0.3)	3.2 (0.5)	3.4 (0.3)
UNA	3.5 (0.3)	5.1 (0.2)	5.0 (0.2)
		0.01 mol kg <sup>-1</sup>	
MF	3.0 (0.3)	4.2 (0.4)	4.5 (0.2)
MC	3.1 (0.2)	4.2 (0.3)	4.3 (0.3)
OP	2.3 (0.3)	3.5 (0.4)	3.4 (0.4)
UNA	3.5 (0.2)	4.9 (0.3)	4.8 (0.4)

<sup>1</sup>Calculated from proton titration data (eq. 10)

<sup>2</sup>Calculated from ion adsorption data (eq. 11)

<sup>3</sup>Uncertainty in p.z.n.c. given is that of the maximum s.d.<sub>Δq</sub> value.

<sup>4</sup>Uncertainty in p.z.n.p.c.<sup>1</sup> is based on the s.d.<sub>ΔH,titr(p.z.n.p.c.)</sub>

<sup>5</sup>Uncertainty in p.z.n.p.c.<sup>2</sup> is based on the larger of s.d.<sub>σ<sub>H</sub></sub> or maximum s.d. Δq.

<sup>6</sup>Values of p.z.n.c. not encountered in the pH range of the experiments. Lower pH limit of experiment is shown.

At a given ionic strength, net proton surface charge density decreased with increasing pH for all soils studied. The values of s.d.<sub>σ<sub>H</sub></sub>, calculated as  $((s.d._{\sigma_{H,titr}})^2 + (s.d._{\sigma_{H,titr}(p.z.n.p.c.)})^2)^{1/2}$  to reflect uncertainty in component terms, were generally in the range 2–6 mmol<sub>c</sub> kg<sup>-1</sup>. The highest values were measured at low pH (Chorover, 1993). The variability in σ<sub>H</sub> measurements increased at low pH because, in this range, very small differences in emf readings between samples translate into large relative differences in the calculated surface proton concentrations. Therefore, an increased data density was required to provide a clear functional description of net proton adsorption at low pH. The titration curves for soils MF, MC, and UNA approached a low pH plateau (below pH 3.5) at low ionic strength, evidently as a result of proton saturation of ionizable surface functional groups. No such plateau was observed for the OP soil.

The slopes of the titration curves for each soil increased with ionic strength and, in the case of soils MF, MC, and UNA, there was an apparent data convergence around pH 3–3.5, which approximately equals the p.z.n.c. value (Table 2) within experimental error. However, only the UNA soil exhibited an obvious common intersection point, i.e., a point of

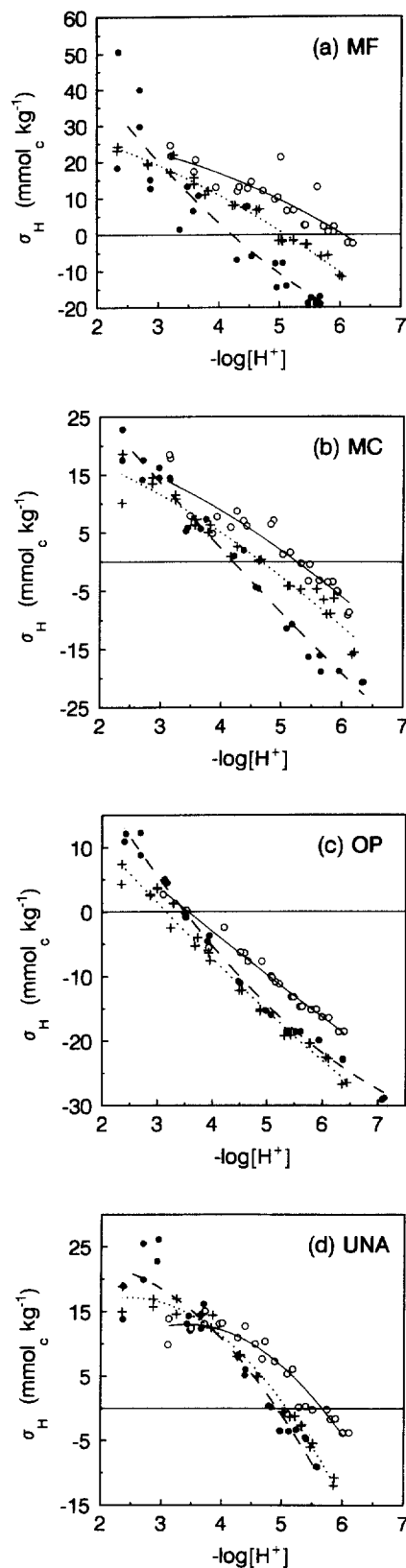


FIG. 2. Net proton surface charge density ( $\sigma_H$ ) vs. pH: (a) MF, (b) MC, (c) OP, (d) UNA. Ionic strength: open circles-0.001 mol kg<sup>-1</sup>; crosses-0.005 mol kg<sup>-1</sup>; filled circles-0.01 mol kg<sup>-1</sup>. Solid, dotted and dashed lines are quadratic regression results for the data at 0.001, 0.005 and 0.01 mol kg<sup>-1</sup>, respectively.

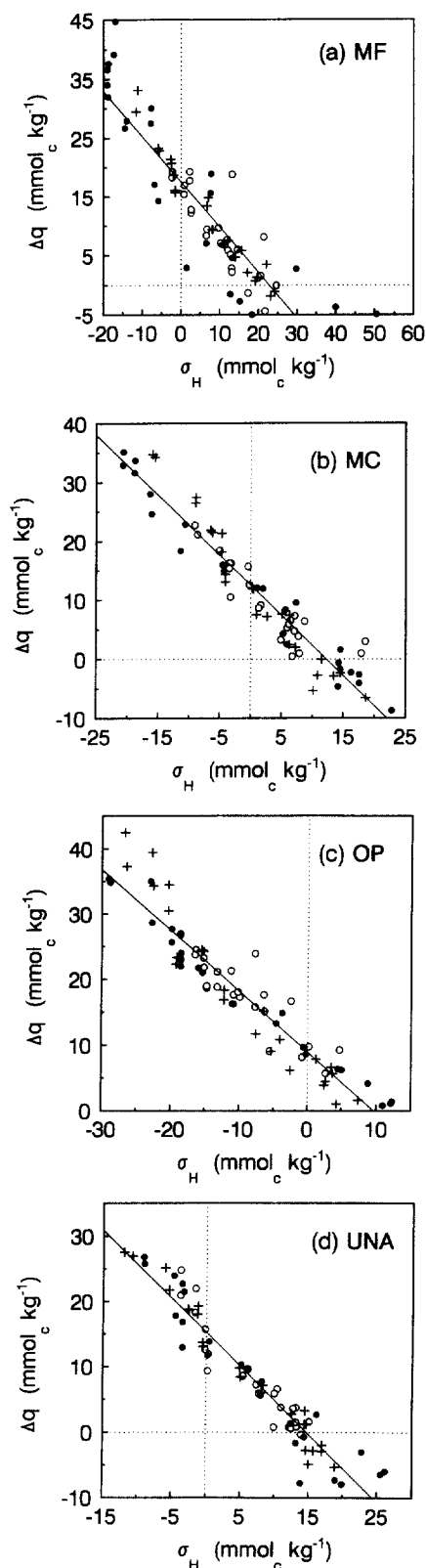


FIG. 3. Net adsorbed ion charge density ( $\Delta q$ ) plotted against net proton surface charge density ( $\sigma_H$ ): (a) MF, (b) MC, (c) OP, (d) UNA. Solid lines are linear regressions over all of the data for a given soil (equations provided in Table 3). Intersection of dotted line indicates origin:  $\sigma_H = \Delta q = 0$ . Ionic strength: open circles-0.001 mol  $\text{kg}^{-1}$ ; crosses-0.005 mol  $\text{kg}^{-1}$ ; filled circles-0.01 mol  $\text{kg}^{-1}$ .

TABLE 3. Linear regression of the data in Fig. 3 on net adsorbed ion charge density ( $\Delta q$ ) vs. net proton charge density ( $\sigma_H$ ). Data at all ionic strengths for a given soil were included in each calculation. Regression slope and intercept confidence intervals ( $p = 0.05$ ) are indicated in parentheses. All  $R^2$  are significant at  $p < 0.0001$ .

Soil	Regression Equation	$R^2$
MF	$\Delta q = -0.77 (\pm 0.09) \sigma_H + 18 (\pm 1.35)$	0.81
MC	$\Delta q = -1.01 (\pm 0.07) \sigma_H + 12.5 (\pm 0.75)$	0.92
OP	$\Delta q = -0.93 (\pm 0.08) \sigma_H + 9 (\pm 1.17)$	0.90
UNA	$\Delta q = -1.04 (\pm 0.07) \sigma_H + 15 (\pm 1.26)$	0.92

zero salt effect (p.z.s.e.). In the case of soils MF and MC, convergence of the curves occurred within one standard deviation of  $\sigma_H$ , which also may be considered a p.z.s.e. within experimental error. The pH values at the data convergence were quite different from the p.z.n.p.c. (Fig. 2). No data convergence was apparent for the OP soil.

The measurement of  $\sigma_H$  by proton adsorption utilized background electrolyte adsorption and structural charge data to establish  $\sigma_{H, \text{int}}$  (p.z.n.p.c.) for each titration curve. Therefore,  $\sigma_H$  as calculated by Eqn. 9 was not independent of the ion adsorption data. However, measurements of ion adsorption were used only to establish a single reference point for the proton adsorption data and, therefore, do not influence the overall shape or slope of the  $\sigma_H$  curves. The  $\sigma_H$  values determined with the help of Eqn. 10 utilized ion adsorption data and are, therefore, fully independent of the proton adsorption measurements. The p.z.n.p.c. values determined using these two approaches were in excellent agreement (Table 2). For all soils except OP a decrease in p.z.n.p.c. with increasing ionic strength was observed (Table 2).

## DISCUSSION

### Surface Charge Balance

Equation 4 can be written in the form

$$\Delta q = (q_+ - q_-) = -(\sigma_H + \sigma_O), \quad (12)$$

indicating that a plot of  $\Delta q$  vs.  $\sigma_H$  should be a straight line with  $x$ - and  $y$ -intercepts both equal to  $-\sigma_O$  and slope equal to  $-1$ , independent of ionic strength or soil characteristics. Equation 12 provides a very stringent test of charge balance for measurements of surface charge components in respect to the accuracy of any methods used. Data plots corresponding to Eqn. 12 are presented in Fig. 3. The solid line in each graph is the result of linear regression on the complete dataset at all ionic strengths for a given soil. Linear regression equations based on the data are listed in Table 3. They show that the data closely approximate Eqn. 12: a straight line of slope  $-1$  and  $y$ -intercept equal to  $\sigma_O$  (cf. Tables 1 and 2). For soil MF, the slope was of magnitude slightly less than 1, although the correct value of  $\sigma_O$  was predicted. In contrast to some previ-

ous reports (Parker et al., 1979; Marcano-Martínez and McBride, 1989), measurements of surface charge by ion adsorption and proton titration thus were quite consistent. In the present study, permanent negative charge was measured independently of the titration and adsorption experiments, and the measurements of  $\sigma_H$  were corrected for low-pH side-reactions and for the effect of conditions at the start of titration. The independent determination of  $\sigma_O$  is critical to the success of the method. The effects of ionic strength on the curves in Figs. 1 and 2 were removed by plotting adsorbed ion charge vs. the surface charge of the potential-determining ion,  $H^+$ .

Thus, for example,  $\sigma_H$  at any ionic strength can be estimated by measuring  $\Delta q$  at that ionic strength and using Eqn. 12 with a measured value for  $\sigma_O$ . This approach could effectively replace the more time-consuming potentiometric titration method.

### Points of Zero Charge

Several results in the present study may be used to evaluate the often-assumed correspondence between a point of zero charge and the common intersection point of proton titration curves (p.z.s.e.). Corrections of  $\sigma_{H,itr}$  by subtraction of the value of  $\sigma_{H,itr}$  at the p.z.n.p.c. (Eqn. 9) usually were significant and the value of  $\sigma_{H,itr}$  at the p.z.n.p.c. was not constant across ionic strengths (Chorover, 1993). Therefore, a common intersection point of the titration curves was not expected a priori (Sposito, 1989b). Only the UNA soil displayed a common intersection point (Fig. 2d), although soils MF and MC exhibited data convergence between pH 3 and 3.5 (Fig. 2a,b). If these regions of data convergence are considered to represent p.z.s.e. values within experimental error, then it is evident that these p.z.s.e. values were significantly lower than the p.z.n.p.c. values (Table 2) for the soils.

On the other hand, if  $\partial\Delta q/\partial I = 0$  at the p.z.n.c., then the p.z.s.e. = p.z.n.c. (Sposito, 1989b). Figure 1 and Table 2 show that this condition was in fact achieved for all of the soils, although it was least evident for soil OP, which also showed less variation of surface charge with ionic strength (Figs. 1c and 2c). Thus, the assumption that, in mixtures of permanent and variable-charge solids,  $\sigma_H$  is independent of ionic strength at the p.z.n.p.c. (Uehara and Gillman, 1980; Singh and Uehara, 1986) was not supported by our data; but the assumption that  $\sigma_H$  is independent of ionic strength at the p.z.n.c. (Parks, 1967; van Raij and Peech, 1972; Espinoza et al., 1975; Laverdiere and Weaver, 1977) was not refuted. Either assumption leads to the prediction that, in the presence of negative structural charge, the p.z.n.c. will be lower than the p.z.n.p.c. by an amount related to the magnitude of  $\sigma_O$ . This prediction is consistent with the results in the present study (Tables 1 and 2) and with the principle of charge balance (Sposito, 1989b).

The increase in p.z.n.p.c. with decreasing ionic strength observed for soils MF, MC, and UNA can be explained on the basis of charge balance, given data on the aqueous surface chemistry of the soils. If  $\partial\sigma_H/\partial pH < 0$ , then by Eqn. 10,  $\partial\Delta q/\partial pH > 0$  (recall that  $\partial\sigma_O/\partial pH = 0$ ). If  $\sigma_O < 0$ , then p.z.n.c. < p.z.n.p.c. (Sposito, 1989b). At the p.z.n.p.c.,  $\sigma_H \equiv 0$  and Eqn. 4 becomes

$$\Delta q = -\sigma_O = \text{constant.} \quad (13)$$

If  $\partial\Delta q/\partial I > 0$  above the p.z.n.c. (Fig. 2), then the pH value at which Eqn. 13 applies (the p.z.n.p.c.) will increase with decreasing  $I$ . Thus, for solid mixtures containing some net permanent charge, the p.z.s.e. will not coincide with the p.z.n.p.c. unless  $\partial\Delta q/\partial I = 0$  at the p.z.n.p.c.

For soil OP, the trend in  $\Delta q$  and  $\sigma_H$  with ionic strength was less clear (Figs. 1c and 2c). There was a convergence of the net adsorbed ion charge data at pH 4, and the  $\Delta q$  functions were identical below pH 4 (Fig. 1c). There was an intersection point at the p.z.n.p.c. between the titration curves at the lowest and highest ionic strengths, although the intermediate ionic strength data did not show an obvious crossover with these curves (Fig. 2c). In this case,  $\partial\Delta q/\partial I = 0$  at the p.z.n.p.c. (p.z.n.p.c. < 4, as shown in Table 2) and data conformed to charge balance (Fig. 3c, Table 3).

### Surface Charge Trends

An increase in pH dependence of both background ion adsorption and proton adsorption with increasing ionic strength is commonly observed for amphoteric solids suspended in indifferent background electrolyte solutions (Davis and Kent, 1990). This effect was clearly observed for soils MF, MC, and UNA (Figs. 1 and 2). In these soils, the adsorption of  $Li^+$  (a strongly hydrated, indifferent cation) dominated the  $q_+$  term (Chorover, 1993). The OP soil, by contrast, showed significantly higher pH dependent adsorption of  $Ca^{2+}$ ,  $Mn^{2+}$ , and  $Mg^{2+}$  than the other three soils (Chorover, 1993). The sum of the bivalent cation contributions to adsorbed cation charge was even greater than that of  $Li^+$  in the acid range of the titrations at 0.001 and 0.005 mol  $kg^{-1}$  ionic strength, although the solution concentrations of the bivalent cations did not significantly affect the ionic strength. The source of these ions is unclear, considering the efficiency of the washing procedures associated with preparation of the soil paste. It is possible that the ions were a result of dissolution processes, or that dispersion of microaggregates during the titration exposed sites previously unexposed (Chorover and Sposito, 1994). Bivalent cations are more likely to form inner-sphere surface complexes than is  $Li^+$  (Breeuwsma and Lyklema, 1973; Sposito, 1984). Charlet and Sposito (1989) observed that the adsorption edges of  $Ca^{2+}$  for a tropical soil rich in Fe and Al oxides were independent of ionic strength. They applied the triple layer model (Yates et al., 1974; Davis et al., 1978) to their data and found that they were best described by assuming that  $Ca^{2+}$  formed unidentate, inner-sphere surface complexes. Thus, that relatively large quantities of bivalent ions were adsorbed by the OP soil is consistent with the apparent ionic strength independence of both  $\Delta q$  and  $\sigma_H$ .

Inner-sphere surface complexation of cations also is thought to depress the p.z.n.p.c. (Stumm, 1992) and may explain, in part, the observed low p.z.n.p.c. of the OP soil (Table 2). However, the p.z.n.c. also was much lower than those for the other soils, even though the OP soil contained the smallest net negative structural charge density (Table 1). The prevalence of  $Mn^{2+}$  in the OP titration solutions suggests that a strongly acidic Mn oxide may be creating the low points of zero charge for this soil (Balistriieri and Murray, 1982).

The p.z.n.c. and p.z.n.p.c. values for soils MF, MC, and UNA were quite comparable (Table 2), although the two soils



differ in organic matter and Fe and Al oxide content (Table 1). The p.z.n.p.c. values are lower than reported values for Fe and Al oxides (Stumm, 1992) and are more similar to that of kaolinite. Ferris and Jepson (1975) observed a p.z.n.c. of 4.8 for NaCl-saturated kaolinite, close to their measured value for the isoelectric point (i.e., p., pH value at zero electrophoretic mobility) of 5.1 in 1.0 mmol dm<sup>-3</sup> NaCl solution. The p.z.n.c. values obtained for kaolinitic soils in the present study were 1–2.5 pH units lower than that reported by Ferris and Jepson (1975), probably as a result of both negative structural charge and ionized organic surface functional groups in the soils (Table 1).

Although Fe and Al oxide coatings have been reported to increase the slopes of titration curves (and p.z.s.e. values) for kaolinite (Hendershot and Lavkulich, 1983), the p.z.s.e. values and slopes of the titration curves in the present study appear to be independent of crystalline Fe and Al oxide content, within experimental precision (Table 1 and Fig. 2). The increase in p.z.n.p.c. value for the UNA soil at higher ionic strength may result from Fe and Al oxides, although this trend was not consistent across ionic strengths (Table 2). Charlet and Sposito (1987) applied the titration-electrolyte-adsorption approach used in the present study and measured p.z.n.p.c. = p.z.s.e. = p.z.n.c. = 4.2 for a kaolinitic Brazilian Oxisol essentially devoid of permanent charge (Anderson and Sposito, 1991). The p.z.n.c. values obtained for similar soils in the present study were lower than that reported by Charlet and Sposito (1987), evidently because of negative structural charge (and MnO<sub>2</sub> in the case of soil OP). The p.z.n.p.c. values at 0.01 mol kg<sup>-1</sup> ionic strength were close to 4.2 for soils MF and MC, lower for soil OP and slightly higher for soil UNA. At lower ionic strengths, p.z.n.p.c. values for soils MF, MC, and UNA were all higher than 4.2 because of permanent charge.

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