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 Keng, J. Ching-win; Uehara, Goro

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## Chemistry, Mineralogy, and Taxonomy of Oxisols and Ultisols<sup>1</sup>

J. C. W. KENG AND G. UEHARA<sup>2</sup>

### ABSTRACT

Ultisols and Oxisols of the tropics frequently contain minerals of the constant surface potential type. The surface charge density of minerals of this type varies with pH and salt concentration. The fundamental electrochemical parameter for minerals of this type is the zero point of charge. The zero point of charge is the pH at which the net surface charge is zero. For pH values more acid than the zero point charge, the sign of the electrical charge is positive. The sign is negative for pH above the zero point of charge.

For soils containing constant surface potential colloids, the zero point generally falls between pH 4-6. The zero point of charge is higher in Oxisols than in Ultisols and generally increase with depth in Oxisols.

The buffering capacity of oxidic minerals increases with increasing pH as predicted by theory. Implications of this property to liming of soil of the tropics is discussed. The effect of anion adsorption on cation retention is also discussed.

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<sup>2</sup>Graduate student and Soil Scientist, respectively.

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The fine fraction of soils can be categorized on the basis of electrochemistry into colloids with constant surface charge, or colloids with constant surface potential. Colloids with constant surface charge include the familiar layered silicates which derive their surface charge from ion substitution in lattice interior. They are frequently called minerals with permanent charge.

Colloids with constant surface potential are equally well known, but have not been studied as extensively as the layered silicates. They include the crystalline and non-crystalline oxides and hydrous oxides of aluminum, iron, titanium, manganese and silicon, as well as several important layered silicates and their amorphous chemical equivalents. Kaolinite, halloysite, allophane and most probably talc and pyrophyllite fall in this category. Quartz, the most abundant mineral in soils also belongs to this group. The mechanism of charge origin for minerals of this type is illustrated in Fig. 1.

In the temperate regions where most soils research is conducted, the predominant soil minerals are those

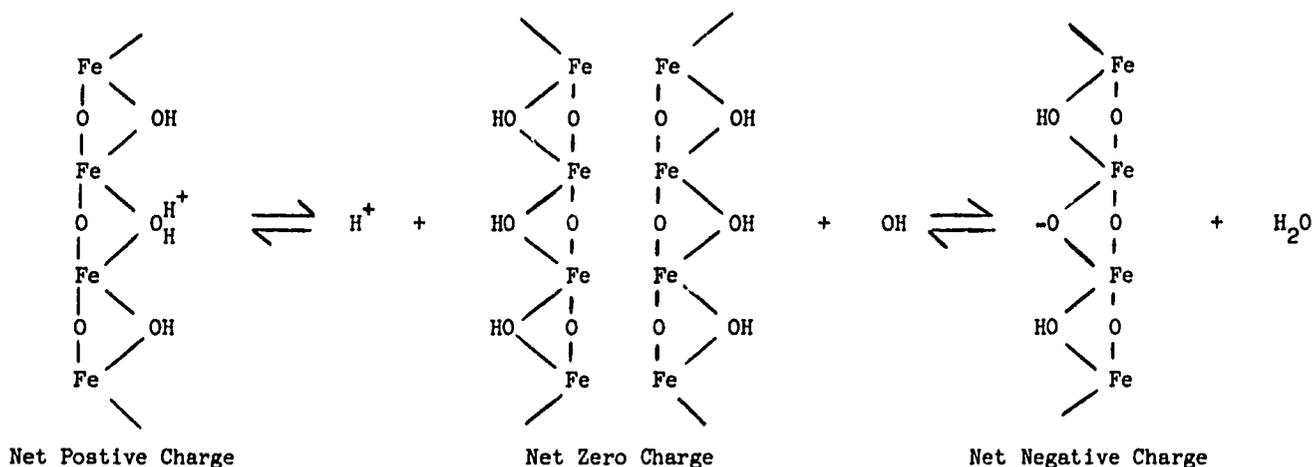


Fig. 1.—Origin of surface charge for a constant potential colloid (eg. hematite) through protonation and deprotonation of surface hydroxyls.

with constant surface charge. Management parameters developed and based on soils containing this group of minerals apply throughout the world, including the tropics, when the chemistry of the soil minerals are of the constant charge type.

If we study the Oxisols and Ultisols of the tropics we discover that minerals of the constant surface potential type are quite common and often the only type present in a soil. In fact the oxic horizon, by definition, cannot contain large quantities of clay with permanent charge. For this reason Oxisols generally are found on remnants of old geologic surfaces. When the rock contains easily weatherable minerals as in basalts and ultra-basic igneous rock, Oxisols may form relatively quickly. Ultisols which are associated with Oxisols generally occur on steeper slopes and frequently on retreating scarps. Ultisols are therefore younger and often contain more minerals of the permanent charge type. In some instances, closely associated Oxisols, Ultisols, and even Alfisols are mineralogically indistinguishable.

For purpose of predicting soil behavior it is helpful to separate minerals into the groups discussed earlier. Soil management parameters developed through research and experience on one group of mineral soils do not necessarily apply to the other. Most soils contain a mixture of constant charge and constant potential colloids. These soils can be adequately managed by modification of parameters based on either group. Serious difficulties arise when experience based on one group is extrapolated to soils containing minerals which are predominantly of the other type. Many of the problems encountered in tropical agriculture are a result of this practice. There is a need to examine soils and soil materials for which well-established management practices do not apply.

The separation of minerals into constant surface charge and constant surface potential type begins with the Gouy-Chapman double layer equation.

$$\sigma_0 = \left( \frac{2n\epsilon kT}{\pi} \right)^{1/2} \sinh \frac{ze\psi_0}{2KT} \quad (1)$$

where  $\sigma_0$  is the surface charge density,  $n$  is the concentration of the equilibrium solutions in number of ions per  $\text{cm}^3$ ,  $z$  is the valence of the counter ion,  $\epsilon$  is the

dielectric constant of the medium,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\psi_0$  is the surface potential.

For low surface potentials ( $\psi_0 \ll 25\text{mV}$ ) equation 1 reduces to

$$\sigma_0 = \frac{K\epsilon}{4\pi} \psi_0 \quad (2)$$

where  $K$  is the reciprocal of the double layer thickness and is a function of electrolyte concentration. For brevity and ease of discussion, equation 2 will be used.

In constant surface charge systems, such as vermiculite or montmorillonite suspended in an aqueous solution, increasing the salt concentration (and therefore  $K$ ), will result in a reduction in surface potential  $\psi_0$ , because  $\sigma_0$  is a constant. On the other hand, the same change in salt concentration will result in a change in surface charge  $\sigma_0$  in constant potential systems. For some constant surface potential colloids,  $\psi_0$  can be held constant by maintaining pH constant. For these colloids,  $\psi_0$  is related to the hydrogen ion concentration through the expression

$$\psi_0 = \frac{RT}{F} \ln \frac{H^+}{H^+_0} \quad (3)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant,  $H^+$  is the hydrogen ion concentration, and  $H^+_0$  is the hydrogen ion concentration at which  $\psi_0 = 0$ .

Equation 2 and 3 can be combined to give

$$\sigma_0 = \frac{K\epsilon}{4\pi} \cdot \frac{RT}{F} \ln \frac{H^+}{H^+_0} = \frac{K\epsilon}{4\pi} (0.059) (\text{ZPC}-\text{pH}) \quad (4)$$

where  $\log \frac{1}{H^+_0}$  is the pH at the zero point of charge (ZPC). Equation 4 shows the relationship between cation exchange capacity ( $\sigma_0$ ) and pH. Colloids which can be described electrochemically by equation 4 are commonly called colloids with pH dependent charge.

The electrochemistry of Oxisols and many Ultisols of the tropics is more adequately described by equation 4 than by assuming constancy of  $\sigma_0$  in equation 1. There are three situations of equation 4 which are of interest.

The first involves the case  $H^+ = H^+_o$  or (ZPC=pH). When this unique situation is met,  $\sigma_o = 0$ . Many fine textured Oxisols, Ultisols, and even Alfisols, have low cation exchange capacities. This simply means that the pH at which CEC was determined was not far from the zero point of charge. Equation 4 also assures us that a low CEC is not necessarily a permanent feature of soils with constant surface potential colloids.

The second situation arises in soils when  $H^+ > H^+_o$  or ZPC > pH. In this situation the surface charge is positive and the soil has a negative cation exchange capacity or anion exchange capacity. This situation more frequently occurs in the subsoil. In this situation the soil pH measured in N KCl is higher than the pH measured in a water suspension.

The last situation involves the case,  $H^+ < H^+_o$  or ZPC < pH. This is normally the case for most surface soils. In this situation a soil material possesses net negative charge and the pH in N KCl will be more acid than the pH in water. In most surface soils, soil solution pH is on the alkaline side of the ZPC, so that the soil is a cation exchanger.

The three cases are graphically illustrated in Fig. 2. In Fig. 2,  $\sigma_o$  is plotted as a function of pH for a low ( $C_1$ ) and high ( $C_2$ ) electrolyte concentration. The slopes of the  $\sigma_o$  - pH curves become steeper with increasing electrolyte concentration. The point of intersection corresponds to the ZPC on the pH axis and net zero charge on the  $\sigma_o$  axis. For an indifferent electrolyte such as KCl or NaCl, all curves will intersect at a single point.

The change in pH with change in salt concentration (more correctly salt activity, a)

$$\left( \frac{dpH}{d \log a_{salt}} \right)_{\sigma_o} = \beta$$

at any value of  $\sigma_o$  is a well-defined quantity for a particular electrolyte.  $\beta$  is the Esin-Markov coefficient (Breeuwsma and Lyklema, 1971) and is a negative quantity when the colloid is negatively charged, zero at the point of zero charge, and positive when the colloid possesses net positive charge.

It is a common practice to measure soil pH in N KCl ( $pH_{KCl}$ ) and again in water ( $pH_{H_2O}$ ). The difference between the pH values

$$\Delta pH = pH_{KCl} - pH_{H_2O}$$

can again take on negative, zero or positive quantities

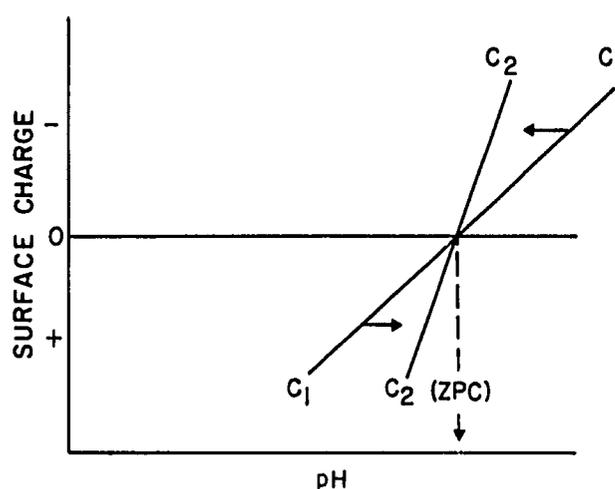


Fig. 2.—Relationship between surface charge  $\sigma_o$ , salt concentration  $C$ , and equilibrium pH for colloids for which  $H^+$  and  $OH^-$  are potential determining ions. When  $\sigma_o$  is positive pH increases with increasing concentration ( $C_2 > C_1$ ). The reverse is true when  $\sigma_o$  is negative.

corresponding to the sign of the net charge on the colloid.

Table 1 provides  $\Delta pH$  values for the Halii and Nipe soils. In both soils the  $\Delta pH$  values begin with positive values in the subsoil and gradually change to more negative values with increasing proximity to the surface. Interestingly the  $\Delta pH$  values are negative when the soil is acid. This suggests that the zero point of charge of the soil colloid is lower in surface horizons than in the subsoil. This shift in ZPCs to lower pH values in the surface horizons is probably due to chemisorption of organic matter. Free organic matter may also contribute to this shift in ZPC.

Laboratory potentiometric titration curves of a powdered iron oxide sheet from a soil are presented in Fig. 3. The minerals identified in this sample were goethite and hematite. The method used to obtain the data was essentially that described by van Raij and Peech (1972). The procedure differed only in that this sample and others shown later were not subjected to acid washing. Serial titration with acid (HCl) or base (NaOH) was made on air-dried samples with no other pretreatment. The supporting electrolyte was  $CaCl_2$ , NaCl or  $Na_2SO_4$ .

Unlike the linear relationship between  $\sigma_o$  and pH

TABLE 1.— $\Delta pH$  AND SIGN OF THE ELECTRICAL CHARGE OF THE COLLOIDS IN THE HALII (GIBBERUMOX) AND NIPE (ACROTHOX) SERIES.

Depth in inches	Organic carbon (%)	Halii $pH_{KCl}$	$pH_{H_2O}$	$\Delta pH$	Depth in inches	Organic carbon (%)	Nipe* $pH_{KCl}$	$pH_{H_2O}$	$\Delta pH$
0-13	2.87	4.54	4.98	-0.44	0-11	6.04	4.3	5.1	-0.8
13-23	1.91	5.07	5.27	-0.20	11-18	2.09	4.4	5.0	-0.6
23-30	1.31	5.28	5.23	0.05	18-28	1.33	4.7	5.0	-0.3
30-44	0.99	5.22	5.00	0.22	28-38	0.86	5.7	5.2	0.5
					38-48	0.72	6.1	5.5	0.6
					48-62	0.56	6.4	5.7	0.7
					62-70	0.19	6.7	5.8	0.9

\*Source: Soil Survey Investigation Report No. 12, SCS, USDA in cooperation with Puerto Rico Agr. Expt. Sta.

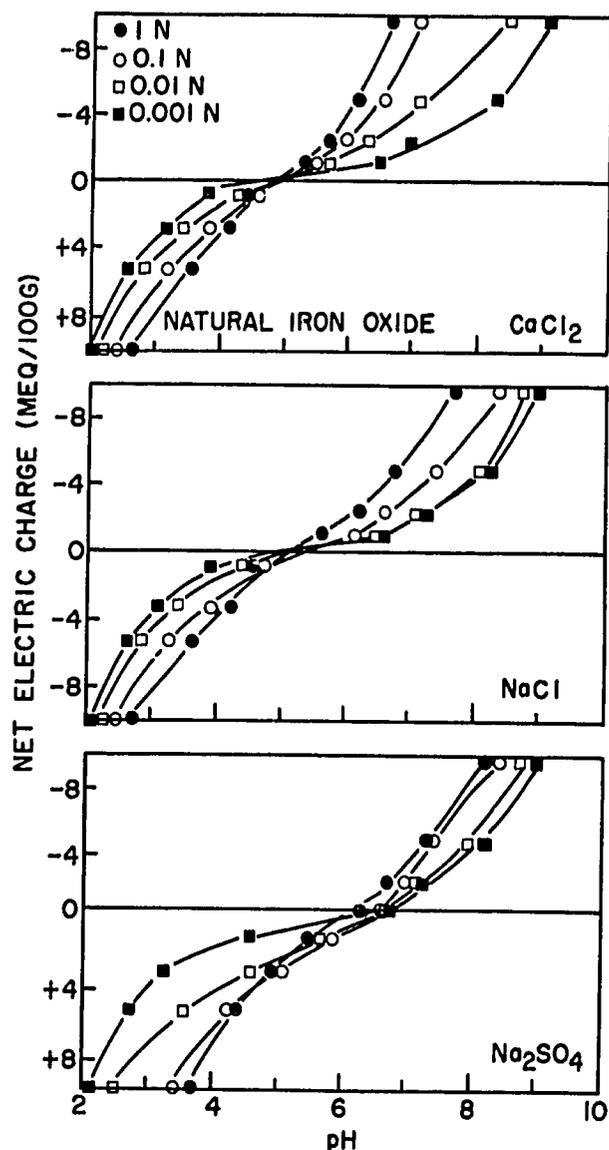


Fig. 3.—Net electric charge of crushed iron oxide sheet as a function of electrolyte concentration and equilibrium pH.

predicted by equation 4, the curves are non-linear. The non-linear relationship is clearly predicted by equation 1. Equation 1 applies in the pH range very near the ZPC, say 0.5 pH units on either side of the ZPC, where the relationship between  $\sigma_0$  and pH can be presumed to be linear. Van Raij and Peech (1972) however, have shown that even equation 1 did not adequately describe their experimental data, but obtained good agreement between experimental and computed surface charge when the Stern modification of equation 1 was used.

The need to invoke the Stern model, and the marked deviation of experimental data from those predicted by the Gouy-Chapman equation suggests that constant surface potential colloids have electrochemical properties quite different from those of the layered silicates. This is especially true when  $\text{CaCl}_2$  or  $\text{Na}_2\text{SO}_4$  is used as the supporting electrolyte instead of  $\text{NaCl}$ . In Fig. 2 we note a change in the shapes of the curves, and in addition, a shift in the zero points of

charge to lower and higher values when calcium and sulfate salts are used.

Theory predicts (Breeuwsma and Lyklema, 1971) that in the absence of specific ion adsorption the change in pH with each ten-fold increase in salt activity is greater in absolute value on the alkaline side of the ZPC for  $\text{NaCl}$  than for  $\text{CaCl}_2$ . Similarly, for a given  $\sigma_0$  on the acid side of the ZPC, the change in pH should be greater with  $\text{NaCl}$  than with  $\text{Na}_2\text{SO}_4$ . The fact that the change in pH is greater with  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_4$  is evidence for specific adsorption of calcium and sulfate ions. In addition the fact that the ZPC has already shifted to lower and higher values with  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_4$  at the lowest (0.001 N) electrolyte concentration suggests that specific adsorption of ions occurs at very low concentrations, and therefore can be important in soil solutions.

$\sigma_0$  — pH curves for several soils are presented in Fig. 4-7. The Haliit soil is a Gibbsiumox and is oxidic in mineralogy, the Molokai is a Torox and kaolinitic, the Paaloa is a Tropohumult and has a mixed mineralogy of gibbsite, kaolinite, anatase, and a mixture of iron oxides plus about 10 percent mica in the clay fraction. The Hilo soil is a Hydrandept and is designated thixotropic in lieu of mineralogy. It is a mixture of gibbsite, organic matter and amorphous hydrated oxides.

The foregoing discussion and laboratory data explains several field observations which are not adequately explained by the constant surface charge theory. These observations include the inordinate amounts of lime needed to raise pH in soils with virtually zero cation exchange capacity, and the increased cation retention when sulfate or phosphate fertilizers are applied to soils. These deviations from expected behavior occur when theory and experience based on soils containing permanent charge minerals are applied to soils whose mineral composition is predominantly of the constant surface potential type.

The experimental  $\sigma_0$  — pH curves clearly show that the buffering capacity (the steepness of the  $\sigma_0$  — pH curves) increases with increasing calcium ion concentration. More important the curves are steeper for calcium than sodium salts and become steeper with increasing pH. This suggests that  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$  is not a particularly efficient chemical for increasing soil solution pH of constant potential colloids. The need to use the Stern-double layer equation (van Raij and Peech, 1972) also suggests that most of the counter ion charge resides in the compact or Stern layer a few angstroms from the colloid surface, and only a small fraction of the total charge is in the diffuse layer. In a sense, the effective charge (the charge in the diffuse layer or total charge minus charge in compact layer) necessary for retention of other cations, and soil dispersion is very small. For this reason some oxidic soils disperse with great difficulty even at high pH's, and possess excellent physical properties in the field. There is also a suggestion that the calcium ions in the Stern layer are held with some affinity, and are not completely removed with a single extraction with neutral salt or  $\text{N NH}_4\text{OAc}$  at pH 7.

The small change in pH upon addition of a large quantity of lime to a soil with low cation exchange capacity, and the inability to account for calcium in readily exchangeable form has sometimes been at-

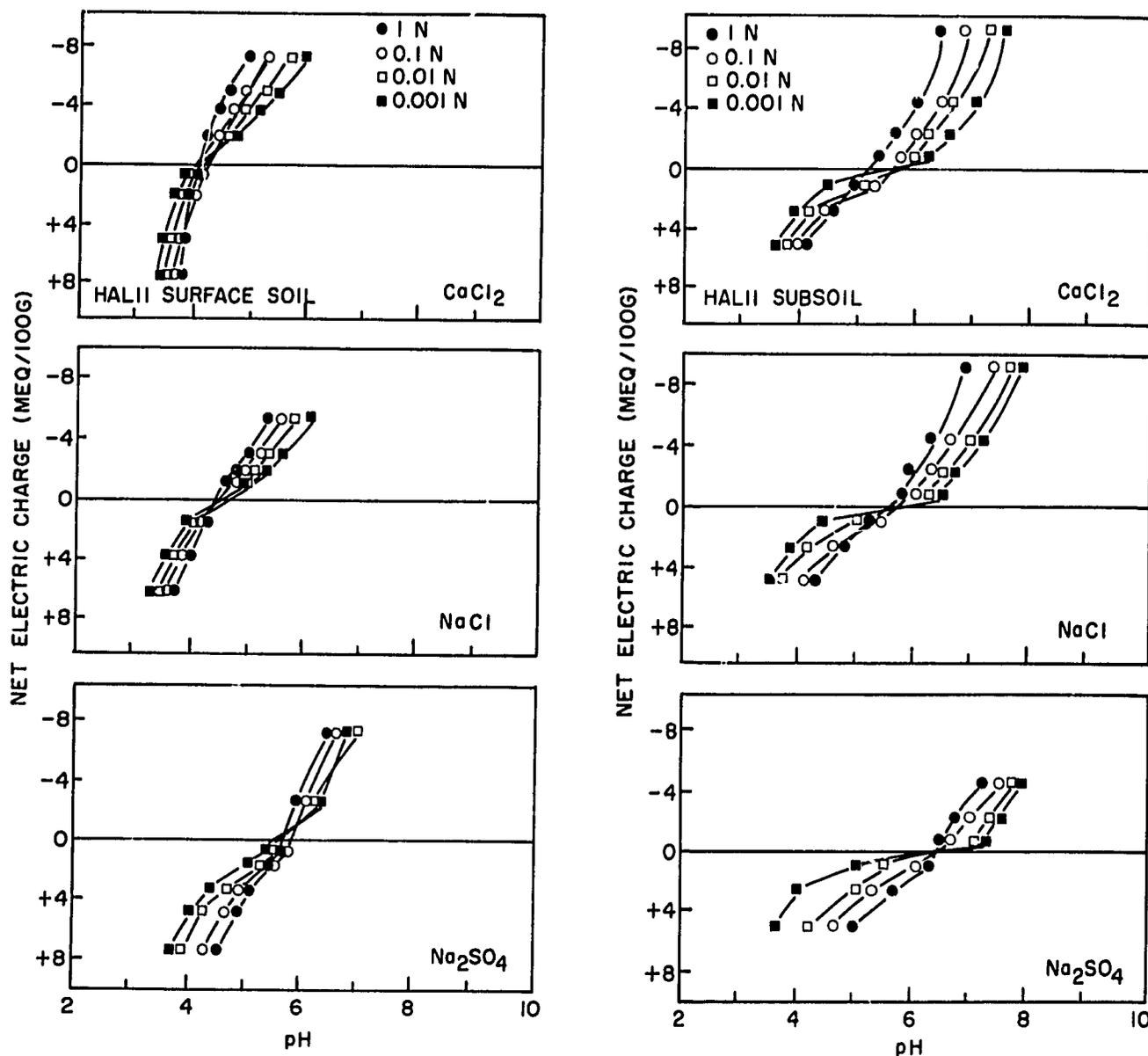


Fig. 4.—Net electric charge of Halii (Gibbsihumox) surface soil (a) and subsoil (b) as a function of electrolyte concentration and equilibrium pH.

tributed to leaching losses. This observation can also be explained by high charge development and strong retention of calcium ions upon application of lime. Interesting and useful research possibilities exist in this area as there are insufficient field and laboratory data to clearly support either view.

If we again examine the  $\sigma_0$  - pH curves in Figures 3 to 7, we note that at the pH's very near the ZPC measured with NaCl, the colloid is rendered positively charged in the presence of sulfate ions. This indicates that sulfate ions, like calcium ions on the opposite side of the ZPC, are efficient generators of surface charge. Since addition of  $\text{Na}_2\text{SO}_4$  increases positive charge, one would expect the cation retention to be reduced. In fact, the reverse effect is observed.

Ayres and Hagihara (1953) showed that addition of  $(\text{NH}_4)_2\text{SO}_4$  to a Hydrandep (see Fig. 6 for  $\sigma_0$  - pH curves) reduced potassium losses due to leaching. This apparent inconsistency has been clarified by

Breuwisma (A. Breuwisma, 1973. Adsorption of Ions on Hematite. Ph.D. Thesis, Agricultural University, Wageningen, The Netherlands) and Breuwisma and Lyklema (1971). They show in their work with hematite ( $\alpha\text{Fe}_2\text{O}_3$ ) that, while specific adsorption of sulfate ions results in a shift of the ZPC to higher pH, and therefore increases the positive charge on the colloid relative to the pH of the ZPC obtained with NaCl, super equivalent adsorption of sulfate ions results in charge reversal. In short, the negative charge in the compact layer exceeds the net positive charge on the oxide surface, so that the counter ions in the diffuse layer are cations.

Phosphate is even more effective than sulfate ion for increasing the cation retention capacity of oxidic materials. Each millimole of sorbed phosphate increases cation retention by about 0.8 me per 100 grams of soil (Mekaru and Uehara, 1972). The greater plant response to  $\text{CaSiO}_3$  than to  $\text{CaCO}_3$  observed in

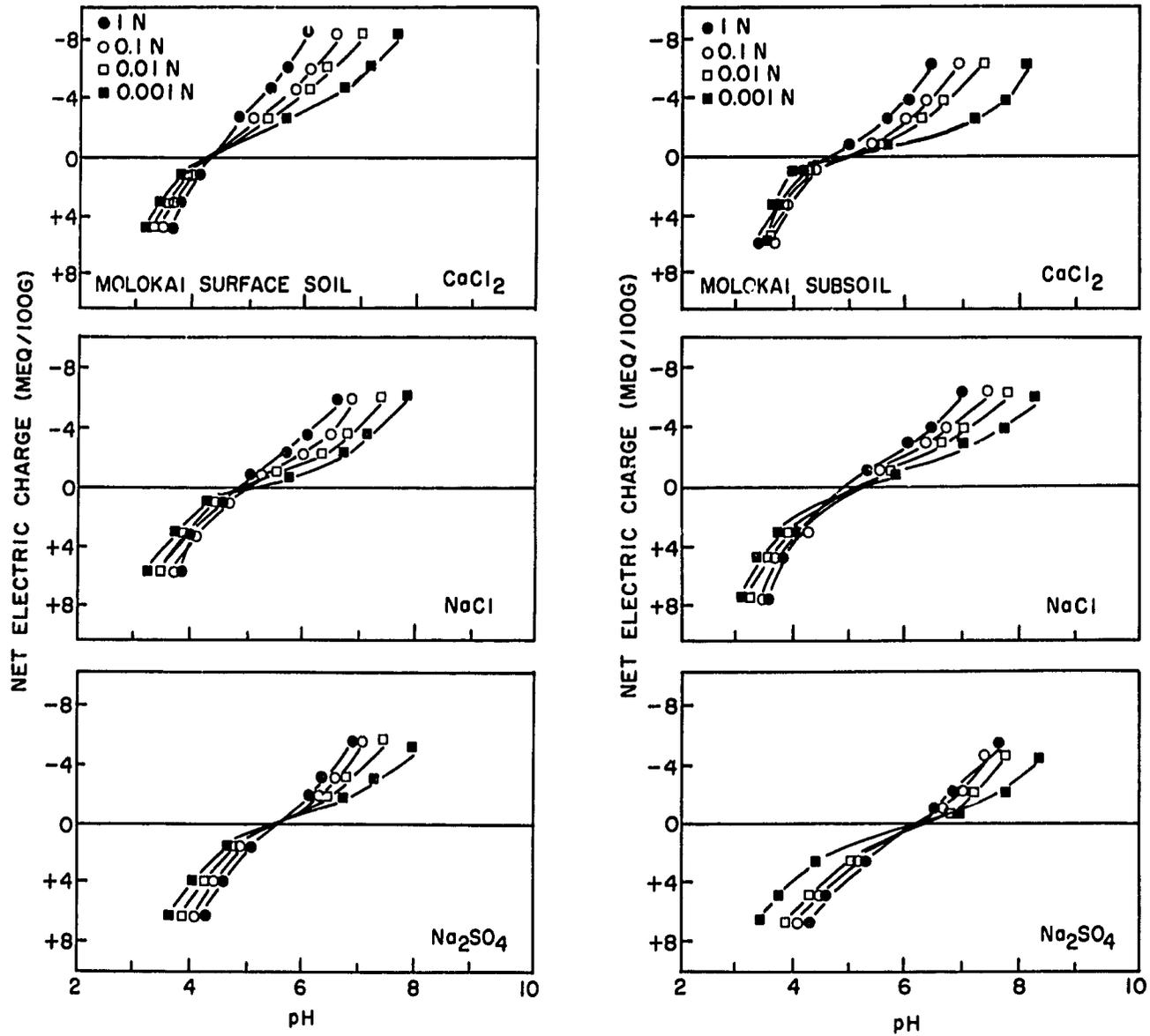


Fig. 5.—Net electric charge of Molokai (Torrox) surface soil (a) and subsoil (b) as a function of electrolyte concentration and

equilibrium pH.

some liming experiments is in part due to the adsorption of silicate ions on the oxide surface and the resultant increased cation retention.

#### SUMMARY AND CONCLUSIONS

Unlike soils of the temperate regions which contain clay minerals of the constant surface charge type, soils of the tropics, particularly the Oxisols and Ultisols, contain minerals which are predominantly of the constant surface potential type. This latter group includes the kaolin minerals, allophane, the crystalline and non-crystalline oxides and hydrous oxides of silicon, iron and aluminum, and organic matter. For these materials, hydrogen and hydroxyl ions are the potential determining ions. The sign and magnitude of the net surface charge on minerals of the constant surface potential group are controlled by soil solution pH. The sign of the charge can be positive, zero,

or negative. When the net charge is zero, the soil or material is said to be at its zero point of charge. For most soils containing minerals of the constant surface potential type, the pH at the zero point of charge ranges from pH 3.5 to 5.0. The pH at the zero point of charge generally decreases with increasing organic matter content, and therefore, the zero points of charge generally increase with increasing soil depth.

Lime application increases net negative charge by deprotonation of surface hydroxyls. Oxides can develop very high surface charge densities, and this accounts for the large quantity of lime required to change soil pH in oxidic soils with virtually zero cation exchange capacity.

Negative surface charge density can also be increased by shifting the zero points of charge to lower pH values. This can be accomplished in the field by addition of organic matter, phosphate fertilizers or silicate amendments.

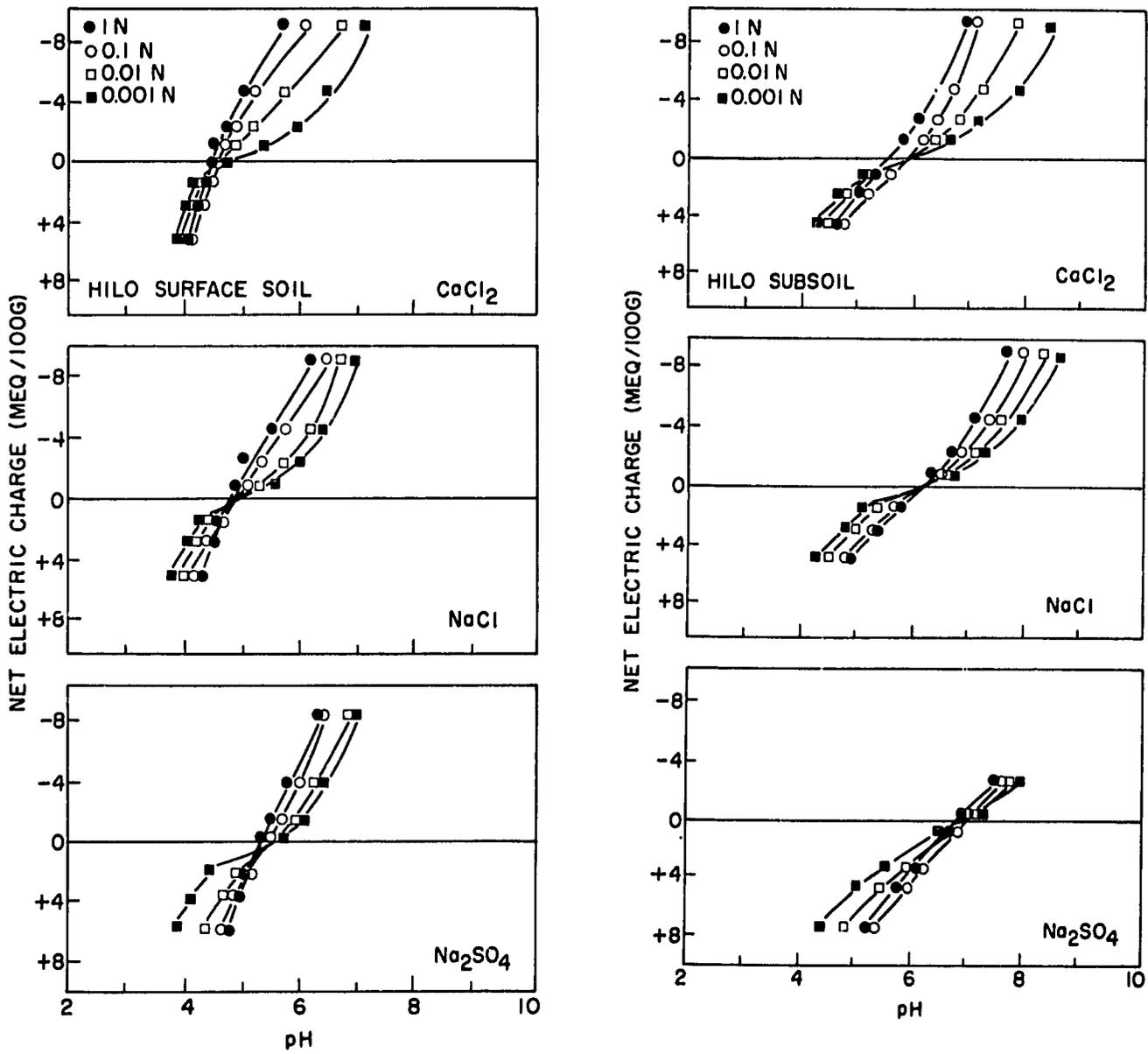


Fig. 6.—Net electric charge of Hilo (Hydrandep) surface soil (a) and subsoil (b) as a function of electrolyte concentration and

equilibrium pH.

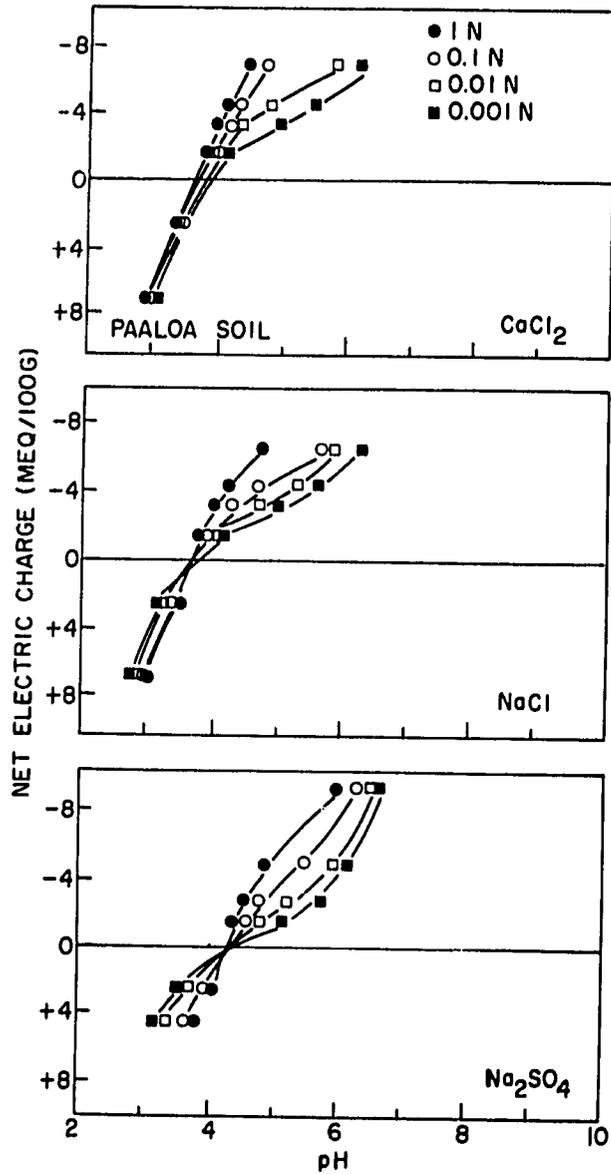


Fig. 7.—Net electric charge of Paaloo soil (Tropohumult) as a function of electrolyte concentration and equilibrium pH.

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