

## ION ADSORPTION MECHANISMS IN OXIDIC SOILS; IMPLICATIONS FOR POINT OF ZERO CHARGE DETERMINATIONS\*

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### ABSTRACT

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In order to clarify the adsorption mechanisms for various ions (e.g., P, K, Ca, Mg), ion adsorption studies were carried out on a range of soils of widely different mineralogical compositions. The soils were classified as: Hydrandep, Gibbsihumox, Eustrtox and Haplustoll and belonged, respectively, to the Honokaa, Halii, Wahiawa and Waiialua soil series in Hawaii.

Soils containing mostly hydrous Fe and Al oxides, thus colloids of the variable-charge type, retain ions through various types of adsorption mechanisms. As a result, certain interactions between cation adsorption and anion adsorption occur which affect the ion exchange processes and thereby the determination of the point of zero charge (PZC).

In this study adsorbed phosphate increased the adsorption of cations and lowered the PZC and adsorbed Ca interfered with PZC determinations unless these were carried out with CaCl<sub>2</sub> as supporting electrolyte. It is likely that this latter interference will have influenced the results of many earlier studies because of the very strong adsorption of Ca by oxidic colloids. In this study only part of the adsorbed Ca could be recovered from the two most highly weathered soils, by repeated extractions with NH<sub>4</sub>-acetate at pH 7.

The results indicate that many soils of the tropics can be characterized effectively by their PZC's. One should be aware, however, of the effects of strongly adsorbed ions commonly present in these soils and thus use those supporting electrolytes for the PZC determinations which counteract these effects.

### INTRODUCTION

Highly weathered soils of the humid tropics, which contain mostly clays of the variable-charge type, possess certain chemical properties which set them apart from less weathered soils in which 2:1 layer silicate clays having a permanent charge prevail. These properties include the following.

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\*The investigations were carried out in the Department of Agronomy and Soils, University of Hawaii, Honolulu, as part of the Ph.D. dissertation of the author.

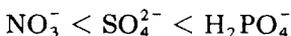
(1) A point of zero charge in the soil pH range where plant growth is possible (Van Raij and Peech, 1972; Keng and Uehara, 1973).

(2) A relatively large anion adsorption capacity (Kamprath et al., 1956; Hingston et al., 1968; Kinjo and Pratt, 1971).

(3) High lime requirements to obtain neutral pH (Matsusaka and Sherman, 1964; Rixon, 1966).

(4) Considerable fixation of cations, particularly Ca (Mikami and Kimura, 1964; Rixon, 1966).

Other studies on anion adsorption by oxidic colloids demonstrated that the adsorption increased according to the following series:



(Kinjo and Pratt, 1971). Moreover, Mearu and Uehara (1972) and Juo and Maduakor (1974) found that strongly adsorbed anions (e.g., phosphates) are associated with increased cation adsorption.

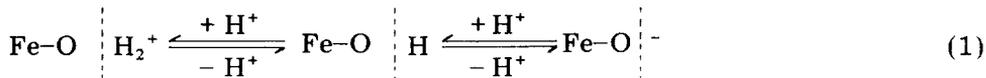
All these phenomena are interrelated. All result from the chemical properties of oxidic colloids. These properties are often difficult to characterize, however, because of their dependence on the pH and ionic composition of the medium in which measurements are carried out.

In this study, the point of zero charge (PZC) rather than the cation exchange capacity at pH 7 is proposed as a criterion to characterize oxidic soils. Moreover, an easy technique was developed for PZC measurements.

## THEORY

Colloids can be separated into two categories on the basis of the origin of surface charges: those with a permanent charge and those with a variable surface charge.

To the variable-charge colloids belong the oxides and hydrous oxides of Fe and Al and the organic colloids. The surface charge on these colloids originates mainly from the association or dissociation of protons with surface hydroxyl groups, as shown for Fe oxides in eq. 1:



Others prefer to interpret eq. 1 in terms of adsorption of  $\text{H}^+$  or  $\text{OH}^-$  ions, the so-called potential determining ions (Parks and De Bruijn, 1962). Subsequently, the surface charge ( $\sigma_0$ ) of variable-charge colloids is defined as:

$$\sigma_0 = F (\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}) \quad (2)$$

in which  $\Gamma_{\text{H}^+}$  and  $\Gamma_{\text{OH}^-}$  are, respectively, adsorption of  $\text{H}^+$  and  $\text{OH}^-$  (mequiv./g) and  $F$  is the Faraday constant. From  $\Gamma_{\text{H}^+} = \Gamma_{\text{OH}^-}$  it follows that the net surface charge  $\sigma_0 = 0$ , which by definition is the point of zero charge (PZC). Moreover, it appears that near the PZC the oxide surface carries three types of active sites:  $-\text{OH}_2^+$ ,  $-\text{OH}$  and  $-\text{O}^-$ ; all of which may contribute to ion adsorption.

Thus for variable-charge colloids, surface charge and ion adsorption are greatly affected by pH and also by salt concentration, valency of counterions and specific adsorption of certain ions, e.g., P adsorption by hydrous Fe and Al oxides. Consequently, surface charge or CEC may not be a useful criterion to characterize soils containing mainly colloids of the variable-charge type.

If, however, the procedure outlined by Breeuwsma and Lyklema (1973) for a hematite system is followed, it may be established that non-contaminated surfaces of variable-charge colloids do possess a characteristic point of zero charge. This PZC is the pH value at which the surface carries a zero net charge, indicated here as  $\text{pH}^0$ .

The value of  $\text{pH}^0$  is often determined from the intersection point of titration curves in the presence of different concentrations of an "indifferent" electrolyte (e.g., NaCl). Presumably, the increase of the electric capacity of the diffuse double layer upon electrolyte increase, for example, will cause an increase of the surface charge on either side of the PZC. Conversely,  $\text{pH}^0$  may be found by comparing the change in pH of suspensions — originally at different pH value — upon addition of the "indifferent" electrolyte. An increase of the pH upon addition of salt then indicates an original pH value below  $\text{pH}^0$ , whereas a decrease occurs for  $\text{pH} > \text{pH}^0$ .

One complication for the above principle is the fact that  $\text{pH}^0$  may be influenced by certain ions. In the case of sesqui-oxides this is in the first place the chemical adsorption of phosphate ions which will shift the PZC to lower pH values. Somewhat more complicated is the action of most divalent cations, which also tends to shift the PZC to lower values, presumably because these ions become specifically adsorbed in a Stern-type layer, even at the PZC of the "uncontaminated" surface. This leads to some release of protons, implying that the PZC in the presence of ions such as Ca will be reached at a lower pH value. Similar processes may occur in the presence of a divalent anion, e.g., sulfate, in which case, however, protons are adsorbed and the PZC is reached at a higher pH.

Another aspect of oxidic colloids, which may affect their ion adsorption and ion exchange, is the presence of microporosity. Both Breeuwsma (1973), working with hematite, and Tsuji et al. (1975), working with highly weathered soils, concluded that such porosity existed.

In the present study, the value of  $\text{pH}^0$  was estimated for a number of oxidic soils after various pretreatments by interpolating to a zero value the pH-shift observed when adding certain electrolytes, as discussed later.

## MATERIALS AND METHODS

### *Soil samples*

The surface soil materials sampled for these studies were developed from different basaltic parent materials under diverse weathering conditions. As a consequence, their mineralogical compositions differ greatly.

TABLE I

Classification and some mineralogical and chemical properties of the experimental soils

Soil series	Waialua silty clay	Wahiawa silty clay	Halii gravelly silty clay	Honokaa silty clay
Soil classification	Vertic Haplustoll	Tropeptic Eustrustox	Typic Gibbsihumox	Typic Hydrandept
Parent material	Colluvium from basaltic rock	Basalt	Basalt	Basaltic volcanic ash
Mineralogical composition	Montmoril- lonite 25-40% Kaolinite 1-10% Amorphous 10-25%	Kaolinite 25-40% Hematite 10-25% Mica 10-25%	Gibbsite 25-40% Goethite 25-40% Kaolinite 1-10% Amorphous gels of Fe and Al oxides 10-25%	Amorphous gels of Fe and Al oxides > 40%
Organic matter (%)	2	3	7	10
Si in saturation extract (ppm)	16	0.9	1.2	2.5
pH (H <sub>2</sub> O)	6.8	5.3	5.2	4.4
Exchangeable cations (mequiv./100 g)				
Ca	24.8	4.0	5.0	3.3
Mg	16.6	1.2	1.7	0.5
K	1.6	0.4	0.3	0.3
Na	1.4	0.2	0.3	0.2
Al	0	0.1	0.1	—
PZC (pH° value) (in CaCl <sub>2</sub> )	< 3.50	3.75	4.00	4.25

The samples were secured from unfertilized sites on experimental farms on the islands of Oahu, Hawaii and Kauai. The classification of the soils and a summary of some mineralogical and chemical properties of the samples are given in Table I.

#### Adsorption studies

Soil samples (3 g on an oven-dry basis) were equilibrated at various pH and P levels for three days (Table II). Subsequently, six different combinations of K and Ca were added in the chloride form, maintaining the overall

TABLE II

Phosphate and pH treatments used for the different soil samples

Soil	Levels of P added ( $\mu\text{gP/g soil}$ )		pH treatments	
Honokaa	1,500	3,000	4.8	5.8
Halii	750	1,500	4.8	5.8
Wahiawa	375	750	4.8	5.8
Waiialua	—	375	—	5.8

chloride concentration at 0.01 *N*. The soil-solution ratio was 1:10. Equilibration with occasional shaking was continued for another 48 h, during which pH was adjusted to 4.8 or 5.8 by adding 0.2*N* HCl. In a separate study, equilibration periods ranging from 2½ to 384 h were compared.

Next, a sample was centrifuged and the supernatant solution analyzed for Ca and K. Cations which disappeared from the solution were considered to have been adsorbed.

Cation recovery was estimated from extracts of four (25 ml) washings with 1*N*  $\text{NH}_4$ -acetate at pH 7. The ratio of Ca : K on the exchange complex, as measured in the  $\text{NH}_4$ -acetate extracts, and the corresponding ratio in equilibrium solutions were calculated and plotted to obtain Ca/K adsorption preference curves.

#### *Determination of the point of zero charge by the $\text{pH}^0$ method*

As explained earlier, the point of zero charge may be determined from the value of  $\text{pH}^0$ . To measure  $\text{pH}^0$  a serial titration technique was used: 3 g (oven-dry basis) of sieved, but unwashed, soil samples were equilibrated with NaOH or HCl for several days until the pH remained constant to establish a pH-range of approximately 3.75–7.0. Subsequently, pH measurements ( $\text{pH}_{\text{H}_2\text{O}}$ ) were made using a combination electrode.

Next, 3 ml of a salt solution were added ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  or  $\text{CaCl}_2$ ) to bring the salt concentration of the supporting electrolyte to 0.005 or 0.05*N*. The resulting change in pH ( $\Delta\text{pH} = \text{pH}_{\text{salt}} - \text{pH}_{\text{H}_2\text{O}}$ ) was recorded 3 h later. The results were plotted against the initial  $\text{pH}_{\text{H}_2\text{O}}$  value and the pH value for which  $\Delta\text{pH} = 0$  ( $\text{pH}^0$ ) was determined by interpolation. The reproducibility of the method was within 5%.

The  $\text{pH}^0$  values were determined for all original soil samples at two concentrations of each of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{CaCl}_2$ . Only for the Waiialua sample, which contains mainly constant-charge colloids and has a high base status, was it impossible to obtain a  $\text{pH}^0$  value.

The effects of liming, exchangeable Ca and adsorbed phosphate on  $\text{pH}^0$  values, determined in  $\text{NaCl}$  and  $\text{CaCl}_2$ , were studied on samples of the Halii and Wahiawa soils. All studies were done with rates of liming and phosphate

application that were within or near the fertilizer range commonly recommended for these soils in Hawaiian agriculture.

Low salt concentrations were employed to prevent unnaturally high competition with adsorbed Al. As reported by Keng and Uehara (1973) desorption of Al occurred at 1*N* salt concentrations and caused a drop in PZC.

## RESULTS AND DISCUSSION

### *Cation adsorption processes; interactions with adsorbed phosphate and pH*

The cation adsorption properties of the four different soil samples and the role of the variable-charge colloids in highly weathered soils were investigated using the following experiments: (a) cation adsorption as a function of time; (b) reversibility of cation adsorption by reextraction of adsorbed cations with  $\text{NH}_4$ -acetate at pH 7; and (c) determination of Ca/K adsorption preference curves measured in the presence of 0.01*N* chloride.

With respect to the first two experiments listed above, it was found that Ca and K adsorptions in the Waiialua and Wahiawa soil samples, both containing 1:1 and 2:1 layer silicate clays, were completely reversible processes, equilibrium being reached in less than 2½ h. For the Honokaa and Halii samples, however, which are both rich in hydrous oxides of Fe and Al, equilibration took as long as 48 h, and the subsequent recovery of cations was incomplete. This was most pronounced for the Honokaa sample from which 30% of the adsorbed Ca could not be recovered. For K and Mg these values were in the order of 15–20%.

Both the time-dependent adsorption and the incomplete recovery of

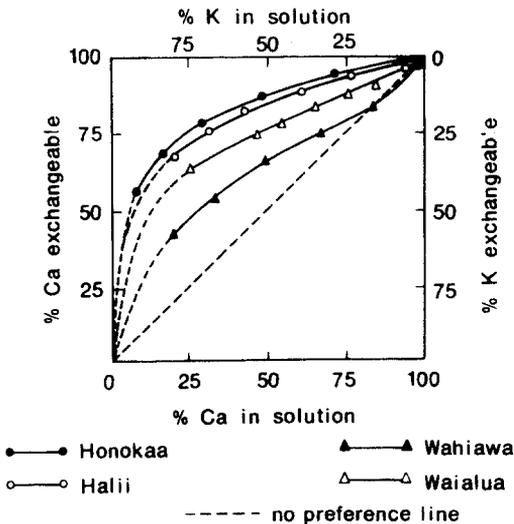


Fig. 1. Cation adsorption preference curves for Ca/K ion pairs as influenced by soil type, when determined in 0.01*N* chloride solutions.

cations could be associated with the microporosity of oxidic colloids, as reported by Breeuwsma (1973) and Tsuji et al. (1975). In addition, it is likely that the  $\text{NH}_4^+$  ions were incapable of exchanging completely with the adsorbed Ca and Mg.

The third experiment gave further evidence in this last direction. Strong adsorption of Ca and to a lesser extent of Mg by oxidic colloids was indicated also by the Ca/K adsorption preference curves (Fig. 1). These curves show that the adsorption preference of Ca over K is greater for the oxidic Honokaa and Halii samples than for the montmorillonitic Waiialua sample. Moreover, the preference for Ca could be enhanced in the oxidic soils by raising the pH of the suspension (Fig. 2) and by phosphate adsorption (Fig. 3). Moreover, the data in Table III demonstrate the effects of adsorbed phosphate on the subse-

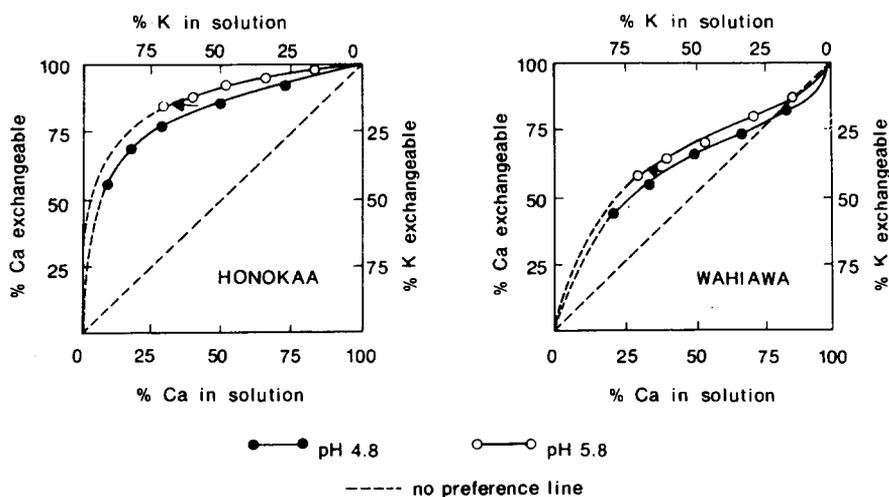


Fig. 2. Cation adsorption preference curves for the Honokaa and Wahiawa soil samples as influenced by pH, when determined in 0.01N chloride solutions.

TABLE III

Effect of adsorbed phosphate added as  $\text{NH}_4$ ,  $\text{H}_2\text{PO}_4$  on Ca and K adsorption from 0.01N chloride solutions at pH 4.8

Soil	P treatment ( $\mu\text{gP/g soil}$ )	m mol P/ 100 g soil	Increase in cation adsorption (mequiv./100 g soil)	
			Ca	K
Honokaa	1,500	4.8	1.90	0.96
	3,000	9.6	3.25	2.19
Halii	750	2.4	1.04	0.28
	1,500	4.8	2.13	0.76
Wahiawa	375	1.2	0.57	0.27
	750	2.4	1.37	0.47

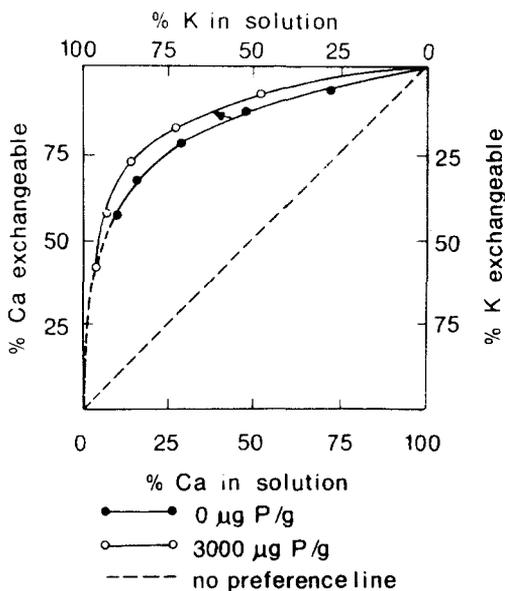


Fig. 3. Cation adsorption preference curves for Ca/K ion pairs for Honokaa soil samples as influenced by adsorbed phosphate, when determined in 0.01N chloride solutions.

quent increases in Ca and K adsorption, the former being at least two times greater. For the Waialua sample, the P adsorption was minor in comparison with the other soil samples and consequently its effect on cation adsorption was insignificant.

To explain these differences in ion adsorption and ion exchange behaviour between the soils, it is useful to distinguish three types of ion adsorption according to increasing strength of the bond between adsorbate and adsorbent: (1) *non-specific adsorption* of monovalent ions, mainly in the diffuse part of the electrical double layer (electrostatic bonding); (2) *specific adsorption* of divalent ions, mainly in the Stern-layer, e.g.,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $SO_4^{2-}$  (electrostatic bonding); (3) *specific adsorption* of ions, directly by the colloid surface, e.g., phosphates (chemical bonding).

It appears that the specific adsorption of divalent ions and phosphates is of particular importance in the case of oxidic colloids (Breeuwsma and Lyklema, 1973), whereas it is only of minor significance in 2:1 layer silicates. These latter have fewer P adsorption sites and generally a much smaller capability of increasing their negative surface charge through proton dissociation. Consequently, phenomena such as incomplete exchange between monovalent and divalent ions and positive interactions between adsorbed phosphate and cation adsorption will be relevant mainly to oxidic soils.

Logical implications are the underestimation of exchangeable cations, particularly divalent ones, when extractions with  $NH_4$ -acetate are made in oxidic soils. As a result the base saturation will be underestimated as well.

Moreover, specifically adsorbed Ca (and probably for similar reasons sulfate) will interfere with PZC measurements in the presence of Na- or K-chlorides, as will be discussed in the following section.

*Point of zero charge (PZC) measurements; effects of specifically adsorbed ions on the PZC*

The cation exchange capacity (CEC), measured at pH 7, is widely used as a criterion for soil characterization and classification. For soils which contain appreciable amounts of variable-charge colloids (e.g., many moderately acid, oxidic soils), however, the CEC is far from stable and measurements taken at pH 7 may thus bear little relevance to reality. In an effort to find a more satisfactory criterion, experiments were run to determine the possibilities of using the PZC of a soil instead. Generally, a low PZC (<3.5) indicates the dominance of layer silicate clays, whereas increasing PZC values reflect an increasing prevalence of variable-charge colloids.

For the PZC to be of predictive value, it ought to be fairly constant. However, depending on the nature of the supporting electrolyte, considerable shifts in PZC have been reported. With  $\text{Na}_2\text{SO}_4$  it moved to higher and with  $\text{CaCl}_2$  to lower values in comparison with  $\text{NaCl}$  (Breeuwsma and Lyklema, 1973; Keng and Uehara, 1973). Similar shifts were observed in the present study (Table IV), but the  $\text{pH}^0$  method used allowed a more detailed evaluation of these shifts than is possible from the common intersection points of potentiometric titration curves. Thus, the effects on the  $\text{pH}^0$  values of lowering the concentration of the supporting electrolyte and of liming or any increase in exchangeable Ca could be determined easily. As shown in Tables IV and V, only the  $\text{pH}^0$  measurements in  $\text{CaCl}_2$  were not affected by these treatments, whereas for  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  considerable increases in  $\text{pH}^0$  occurred.

In case of phosphate adsorption, chemical bonding between adsorbate and adsorbent leads to an increase in the net negative surface charge and a lowering of the PZC. The latter was confirmed for phosphated samples of

TABLE IV

Values of  $\text{pH}^0$  determined for different salts at concentrations of 0.005 and 0.05 N

Soils	$\text{pH}^0$ values					
	$\text{CaCl}_2$		$\text{NaCl}$		$\text{Na}_2\text{SO}_4$	
	0.005 N	0.05 N	0.005 N	0.05 N	0.005 N	0.05 N
Honokaa	4.25	4.25	4.75	4.50	5.40	5.10
Halii	4.05	4.00	5.10	4.80	5.75	5.50
Wahiawa	3.75	3.75	4.60	4.20	5.35	5.20

TABLE V

Effects of liming on  $\text{pH}^0$  values determined in 0.05 *N* solutions of  $\text{CaCl}_2$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  in relation to exchangeable Ca + Mg

Soils	Treatment	Exchangeable Ca + Mg (mequiv./100 g)	$\text{pH}^0$ values		
			$\text{CaCl}_2$	$\text{NaCl}$	$\text{Na}_2\text{SO}_4$
Halii	unlimed	6.66	4.00	4.80	5.50
	limed	8.12	4.05	5.70	6.25
Wahiawa	unlimed	5.13	3.75	4.20	5.20
	limed	10.84	3.80	5.80	6.70

TABLE VI

Values for  $\text{pH}^0$  as determined in 0.05*N* salts for samples previously equilibrated with various rates of calcium and phosphate

Soils	Treatments		$\text{pH}^0$ values	
	added Ca (mequiv./100 g)	added P (ppm)	$\text{CaCl}_2$	$\text{NaCl}$
Halii	0	0	4.10	4.45
	2.7	100	4.10	4.70
	5.3	100	4.10	5.25
	2.7	800	3.80	4.40
	5.3	800	3.90	4.60
	5.3	800	3.90	4.60
Wahiawa	0	0	3.85	4.30
	2.7	100	3.80	4.60
	5.3	100	3.85	5.30
	2.7	800	3.65	4.05
	5.3	800	3.65	4.35
	5.3	800	3.65	4.35

the Halii and Wahiawa soils. Again the effect was most clearly reflected by  $\text{pH}^0$  values measured in  $\text{CaCl}_2$  (Table VI).

Although these results may have been influenced by the exchangeable cations present in the samples (see Table I), all these shifts were in the expected directions and can be explained logically by distinguishing between the various adsorption and bonding mechanisms already mentioned.

Most likely, a substantial part of the Ca, whether added or already present in the samples, will be specifically adsorbed in the Stern-layer, a process ruled by the colloid surface charge ( $\sigma_0$ ). Na adsorption, being non-specific, will, however, be the combined effect of both surface charge and counter charge (mainly from Ca) of adsorbed ions in the Stern-layer. Thus, particularly for the Honokaa and Halii samples which retain Ca very strongly, a  $\text{pH}^0$  measure-

ment in  $\text{CaCl}_2$  is more likely to indicate the PZC than similar measurements in  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$ . This conclusion is supported by the measurements on phosphated samples, which indicated a lowering of the PZC by 0.2 to 0.3 pH units (determined in  $\text{CaCl}_2$ ), due to the adsorption of 800 ppm P (Table VI).

The investigated problems arise largely from the presence of both positive and negative charges over a fairly wide pH range above and below the PZC (Breeuwsma, 1973). Consequently, both anion and cation adsorption will occur simultaneously over that pH range and will be interdependent. This interdependence, as well as the specific Ca adsorption, will equally affect the outcome of PZC measurements, whether done by potentiometric titrations or by the proposed  $\text{pH}^0$  method. Not taking into account these factors may lead to considerable confusion in the possible use of PZC values for soil characterization purposes.

In any case, more experimentation on different soils will be required to test the method and the effects of various mixtures of different types of adsorbents. Eventually, this may result in a better appreciation of the distinctive chemical properties of oxidic soils due to their variable-charge type colloids. Not only would then a better characterization of these soils be possible, but some practical indications on soil fertility management aspects, such as liming and phosphate fertilization could well follow.

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