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Batch 72

1. SUBJECT CLASSIFICATION

A. PRIMARY
Food production and nutrition AF22-0000-GG50

B. SECONDARY
Soil chemistry and physics--Tropics

2. TITLE AND SUBTITLE
Surface and charges characteristics of selected soils in the tropics

3. AUTHOR(S)
Gallez,A.; Juo,A.S.R.; Herbillon,A.J.

4. DOCUMENT DATE	5. NUMBER OF PAGES	6. ARC NUMBER
1976	9p.	ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS
IITA

8. SUPPLEMENTARY NOTES *(Sponsoring Organization, Publishers, Availability)*
(In IITA j.ser.57)
(In Soil Soc.of Am.j.,v.40,no.4,p.601-608)

9. ABSTRACT

10. CONTROL NUMBER
PN-AAE-613

11. PRICE OF DOCUMENT

12. DESCRIPTORS
Adsorption
Anions
Cations
Nigeria
pH
Surface properties
Tropics

13. PROJECT NUMBER

14. CONTRACT NUMBER
AID/ta-G-1185 GTS

15. TYPE OF DOCUMENT

AID 590-1 (4-74)

AID/ta-G-1185 GTS
IITA
PN-AAE-613

reprint series

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References:
IITA Journal Series 57
Soil Science Society of America Journal Vol. 40, 1976

INTERNATIONAL INSTITUTE OF TROPICAL AGRICULTURE
PMB 5320
IBADAN, NIGERIA

Reprinted from the *Soil Science Society of America Journal*
Volume 40, no. 4, July-August 1976
677 South Segoe Rd., Madison, WI 53711 USA

Surface and Charge Characteristics of Selected Soils in the Tropics[1]

A. GALLEZ, A.S.R. JUO AND A. J. HERBILLON[2]

ABSTRACT

Specific surface area and surface charge characteristics of some Alfisols and Ultisols from Nigeria were studied. Specific surface are measured by ethylene glycole retention was generally 2 to 3 times greater than the specific surface area measured by N_2 adsorption for both surface and subsoil samples. Soils derived from basalt had the greatest surface area per gram of clay as measured by both methods.

The surface charge-pH curves of the soils bear the characteristic features of metallic oxides, indicating that surface charge behaviour of the soils studied follows the constant potential model. Values of PZC for Alfisol and Ultisol samples ranged from pH 3.0 to 3.9. Subsoils generally have higher PZC than corresponding surface horizons. Specific adsorption of sulfate resulted in a shift of the PZC to a higher value and an increase in the magnitude of positive charge.

Cation and anion retention measurements showed that soils derived from basement complex rocks and sandstones contain negligible amount of positive charge while soils from basalts bear moderate amount of positive charge at their natural pH condition. Evidence also indicated that the Alfisols and Ultisols bear a small amount of permanent negative charge ranging from 1 to 4 meq/100 g.

The limitation of using CEC value determined by conventional procedures as a criteria for soil taxonomy is discussed.

Additional Index words: **specific surface area, point of zero charge (PZC), Alfisols, Ultisols, kaolinite.**

[1]Int. Inst. Tropical Agriculture (IITA) J. Paper no. 57, Received 17 Nov. 1975. Approved 3 Mar. 1976.

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ONE OF THE major features of many highly weathered soils in the tropics is the predominance of kaolinite, Fe and Al oxides and hydrous oxides in the clay fraction. In contrast with smectite and vermiculite, these minerals normally do not bear any appreciable amount of permanent negative charges. The magnitude and the sign of the surface charge of oxide minerals depend not only upon pH, but also upon the nature and concentration of electrolytes present in the soil solution.

Parks and de Bruyn (1962) distinguished two types of electrical double layer on the basis of the mechanism by which free charges are distributed across a solid-solution interface; (i) a reversible double layer which exists on surface bearing constant potential, and (ii) a completely polarizable double layer which exists on surfaces bearing constant charge. The constant potential model applies to soil minerals such as oxides and hydrous oxides of Fe and Al while the constant charge model applies to layer silicate minerals such as smectite and vermiculite which bear permanent negative surface charges due to isomorphous substitution (Keng and Uehara, 1973; van Raij and Peech, 1972). The most convenient reference for predicting the charge dependent behavior of oxide minerals is the point of zero charge (PZC). The PZC of an oxide minerals is the pH at which the net surface charge from all sources is zero (Parks, 1967). The PZC, however, is not a unique parameter for a particular oxide/solution interface as such because it may be af-

Table 1—Classification and Clay mineralogy of soils studied.

Soil and horizon	Depth, cm	Classification	Parent material	Mineral in clay fraction†
Ekiti-A1	0-16	Paralithic Ustropept	Banded Gneiss	K, H, M, Gh
Ekiti-C	46-66	Paralithic Ustropept	Banded Gneiss	K, H, M, Gh
Egbeda-A1	0-6	Oxic Paleustalf	Banded Gneiss	K, M, Gh, Hm
Egbeda-IIB2t	16-63	Oxic Paleustalf	Banded Gneiss	K, M, Gh, Hm
Egbeda-IIIB3t	103-152	Oxic Paleustalf	Banded Gneiss	K, Gh, Hm
Itagunmodi-B2	60-150	Oxic Paleustult	Amphibolite	K, Hm, Gh
Araromi-B2t	65-110	Rhodic Paleustalf	Amphibolite	K, Gh, Sm
Alagba-B1	36-68	Oxic Paleustalf	Coastal Sediments	K, Gh, Hm
Nkpologu-B21t	43-70	Oxic Paleustult	Sandstone	K, Gh, G, Hm
Ikom-Ap	0-7	Orthoxic Tropohumult	Olivine Basalt	K, Gh
Ikom-B21t	26-69	Orthoxic Tropohumult	Olivine Basalt	K, Gh
Ngala	0-15	Vertisol	Alluvium	K, Sm

† K—kaolinite; H—halloysite; M—dioctahedral mica; Gh—goethite; Hm—hematite; G—gibbsite; Sm—smectite.

fected by the composition of the solution with which it is in contact (Breeuwsma and Lyklema, 1973).

van Raij and Peech (1972) reported on the surface charge-pH curves of some Alfisols and Oxisols from Brazil and concluded that the electrochemical behavior of the soils studied was similar to that exhibited by many metallic oxides. Keng and Uehara (1973) showed that the PZC of some Oxisols and Ultisols from Hawaii generally falls between pH 4 to 6 and that the PZC is higher in Oxisols than Ultisols.

Interactions among amorphous materials and crystalline minerals in the clay fraction may result in certain modification of the surface and charge characteristics of the soil system. Greenland and Oades (1968) and Greenland (1976) showed that kaolinite-synthetic goethite complexes formed under alkaline conditions were merely mechanical mixtures and that the kaolinite surfaces did not become coated by iron hydroxide. The magnitude of the positive charge increases in proportion to the amount of goethite in the system. However, when Fe hydroxide was precipitated on kaolinite surface at pH 3, sorption of the positively charged Fe hydroxide particles on kaolinite surfaces occurred causing the reduction of both the specific surface area and the permanent negative charges of the complex.

Although the soil is a much more complex system, from electro-chemical point of view it may be treated as a mixed-system composed of constant potential and constant charge surfaces existing in various proportions. In many highly weathered upland soils in the tropics, the constant potential colloids, such as Fe and Al oxides, certainly play a dominant role in influencing the physical and chemical properties. Thus a better understanding of the physicochemical behavior of soils rich in oxides and kaolinite should lead the development of better management practices for soils in the humid tropics.

This paper reports the surface and charge characteristics of selected soils in southern Nigeria. These soils are representative of a wide range of parent materials and weathering conditions in the humid region of West Africa.

MATERIALS AND METHODS

Soil and Clay Samples

The classification, mineralogy, and other physical and chemical properties of the soils used in this study are given in Tables 1 and 2. Detailed clay mineralogical studies of soils have been reported by Gallez (1975) with the exception of the two soils derived from amphibolite and a Vertisol (Ngala). The soils were air dried and passed through a 2-mm sieve. Kaolinite samples were obtained from Wards Natural Sciences Co. X-ray analysis showed that the samples contained a small amount of mica. Organic C content was determined by dichromate oxidation (Allison, 1965, p. 1372–1375). Effective CEC was determined by summation of neutral 1 *N* NH_4OAc exchangeable bases and 1 *N* KCl exchangeable Al and H (McLean, 1965, p. 986–988). Free Fe and Al oxides were determined using dithionite-citrate system buffered with sodium bicarbonate (Mehra and Jackson, 1960).

Surface Areas

Specific area was obtained from the BET-nitrogen adsorption isotherm at −196°C and by a gravimetric method based on the retention of ethylene glycol monoethyl ether (EGME) using soil samples previously dried over P_2O_5 (Heilman et al., 1965). Prior to the N_2 adsorption measurement, air-dried soil samples were degassed with a flow of helium at 80°C for 12 hours. Data obtained following this pretreatment were in close agreement with data following pretreatment by evacuating samples at 105°C. The BET-specific surface areas were determined on a Perkin Elmer model 212D Sorptomer using a continuous flow method.

Potentiometric Titrations

The procedures described by van Raij and Peech (1972) was used. A series of 4 g, H-saturated soil samples (2 g for H-kaolinite) was equilibrated with known amounts of acid (HCl) and base (NaOH) in various concentration of NaCl for 3 days in a closed humidified glass container to prevent evaporation. The pH of the supernatant solution was determined using a Beckman Expandometric pH meter with micro glass electrodes and a recorder. The amount of H^+ and OH^- ions adsorbed at a given pH value is equal to the amount of HCl and NaOH added after correction for the amount of acid or base required to bring the electrolyte solution alone to the same pH value.

Table 2—Some physical and chemical properties of the soils.

Soils	Clay	Organic carbon	pH (soil paste) H_2O	pH (soil paste) KCl	Effective CEC†	DCB-Fe_2O_3	DCB-Al_2O_3	PZC	Surface area BET-N_2	Surface area EGME
	%	%			meq/100 g	%	%		m^2/g	m^2/g
Ekiti A1	15.3	1.56	6.78	6.26	8.16	1.45	2.39	3.0	3	23
Ekiti C	30.7	0.35	5.95	4.90	4.89	2.26	3.12	3.0	16	42
Egbeda A1	24.0	1.80	6.19	5.60	8.73	5.65	1.19	3.0	13	27
Egbeda II-B2t	53.0	0.78	5.53	4.88	4.67	7.79	1.17	3.3	24	60
Egbeda IIIB3t	47.0	0.02	6.16	6.09	3.89	13.95	1.51	3.5	28	71
Etagunmodi B2	66.0	0.38	4.80	4.50	1.81	13.05	1.53	3.9	41	80
Araromi B2t	57.2	0.27	5.80	5.00	9.85	11.08	0.57	3.5	39	75
Alagba B1	48.2	0.44	5.30	4.00	2.83	4.62	1.34	3.5	18	49
Nkpologu B21t	29.3	0.61	4.76	3.92	1.78	3.86	1.20	3.6	10	27
Ikom Ap	42.0	4.76	5.91	5.04	5.15	8.95	2.61	3.1	40	110
Ikom B21t	74.0	0.60	5.77	4.35	4.97	10.32	3.14	3.6	63	106
Ngala A1	62.2	0.86	6.70	5.50	34.84	0.32	0.73	2.6	22	222
Kaolinite	--	--	--	--	--	--	--	2.8	18	18

† Effective CEC was determined by the sum of *N* N_4OAc exchangeable bases and *N* KCl exchangeable Al and H.

The net surface charge or adsorption density, $\Gamma H^+ - \Gamma OH^-$, is then plotted against the equilibrium pH of the system. The PZC of the soil is taken as the pH value where the charge-pH curves measured in different electrolyte concentrations intersect one another (Parks and de Bruyn, 1962). The charge-pH curves and corresponding PZC's were also determined in $MgCl_2$ and K_2SO_4 for selected soils.

Determination of Electric Charges

Positive and negative charges in soil were determined measuring cation and anion retention according to the Schofield method (1949) as described by van Raij and Peech (1972).

The procedure involves saturating a series of 4 g soil samples with 1*N* NaCl solution, adjusting the pH to desired values with NaOH and HCl. After equilibrium is attained, the suspensions were first washed 3 times with 0.2*N* NaCl solution, then 8 times with NaCl of desired concentrations (0.2, 0.05, 0.01*N*) by centrifugation. The solutions were pre-adjusted to desired pH values. Finally, the Na^+ and Cl^- was then extracted 5 times with 0.5*N* NH_4NO_3. Correction was made for the entrapped Na^+ and Cl^- in the equilibrium solution. Sodium was determined on a EEL flame photometer and chloride by potentiometric titration using Beckman chloride electrode. Exchangeable Al in the NH_4NO_3 extracts was determined according to the modified aluminon method (Hsu, 1964).

RESULTS AND DISCUSSION

Specific Surface Area of the Soil

The EGME-surface area is much greater than BET-N_2 surface area for all soils studied (Table 2). This is to be expected in the case of the Ngala soil (a Vertisol) which contains a substantial amount of smectite. However, remaining soils do not contain any detectable amount of 2:1 type swelling clays (Gallez et al., 1974). The difference in surface area by the two methods for the surface horizons may be partly due to soil organic matter. However, the large differences in the subsoil samples cannot be attributed to the presence of organic matter alone. This is particularly true in the case of the $IIIB_3t$ horizon of the Egbeda soil which contains negligible amount of organic matter, yet the EGME-surface is larger than that by BET-N_2 by a factor of 2.5.

Electron microscopic observations (unpublished data) of the clay fraction of Ikom subsoil samples showed the presence of some gel-like and imogolite-like materials. The smaller surface area measured by the BET-N_2 method on these samples may thus be partly due to the surface loss of the gel-like material as a result of drying. However, this explanation does not apply to the other subsoil samples which also show an EGME-surface area approximately two times greater than the BET-area; i.e. plotting the BET-area against the EGME-area of these samples gave a linear relationship (not shown). These results suggest that there may be two layers of EGME molecules adsorbed on the oxide surface with the first layer possibly held by chemi-sorption, or specific adsorption. However, it is difficult to conclude at this point whether the discrepancy in specific surface area is due to an underestimation by N_2, or overestimation by EGME. Further studies are being conducted to clarify this point.

An attempt was also made to characterize the interaction of Fe oxides and kaolinite in soils by measuring the BET-N_2 surface area of the sample before and after treatment with dithionite–citrate–carbonate (DCB). The specific surface area due to Fe oxides (*A*) was calculated using the following formula according to Greenland and Oades, (1968),

$$A = \frac{1}{W_{Fe}}[S_O - S_R(1 - W_{Fe})]$$

where *So* is the specific surface area of the untreated sample in m^2/g, S_R is the specific surface area of the sample residue after DCB treatment, and W_{Fe} is the grams of total free Fe oxides per gram of clay.

Table 3—Calculated surface area of Fe_2O_3 in soils.

Sample no.	Soil horizon	Weight of Fe_2O_3 (W_{Fe})	Specific surface area† S_O	S_R	A
		g/g clay	m²/g		
1.	Egbeda B2t	0.15	45	40	73
2.	Ikom B1	0.20	79	42	227
3.	Ikom B21t	0.14	85	46	324
4.	Nkpologu B21t	0.13	34	32	47
5.	Kaolinite	--	18	18	-

† S_O = Surface area of soil clay measured by N_2 adsorption.
S_R = Surface area of residual clay after DCB treatment measured by N_2 adsorption.
W_{Fe} = g of DCB-Fe_2O_3 per g of soil clay.
A = Derived surface area of Fe_2O_3, m^2/g of Fe_2O_3.

Both the specific surface area of the untreated clay (S_O) and the calculated surface area of Fe oxides (*A*) for the two Ikom samples are much larger than for the Egbeda soil even though the total free Fe oxide content is approximately the same for all three samples. This suggests that a large portion of the Fe oxides in the basaltic soil (Ikom) exists in very fine, discrete particles. The magnitude of the calculated Fe oxide surface area of this soil also agrees fairly well with that reported by Greenland and Oades (1968) for synthetic goethite in Kaolinite-goethite mixtures. In the case of the Egbeda soil clay, the relatively lower values of A and S_O suggest a stronger association of the Fe oxides with kaolinite surface resulting in a reduction of total surface area. Electron microscopic observations (Gallez et al., 1974) of the clay samples also support this view. The large masses of electron dense particles of the Egbeda clay indicate Fe coatings exist on the kaolinite surfaces. The differences in Fe oxide-kaolinite interaction in Ikom and Egbeda soil apparently reflect the chemical environment when the precipitation and crystallization of iron oxides took place (Fripiat and Gastuche, 1952; Greenland and Oades, 1968; Habibullah and Greenland, 1971).

The Nkpologu soil showed little change in surface area on DCB treatment even though it contained approximately the same amount of Fe_2O_3 as the other soils. It is possible that the DCB treatment in this case has caused an increase in the specific surface area of the residue clay, thus compensating the decrease due to Fe oxide removal.

Surface Charge-pH Curves

The charge-pH curves for all soil samples measured in the four NaCl concentrations (0.001 to 1*N*) intersect one another in accord with the constant potential model for soil colloids (Fig. 1). These plots were not corrected for exchangeable Al as did van Raij and Peech (1972). The PZC values ranged from pH 2.6 to 3.9 (Table 2). In all cases, the PZC occurred below the natural pH value of the soil indicating that the soil colloids bear net negative charges under natural conditions. This is also in agreement

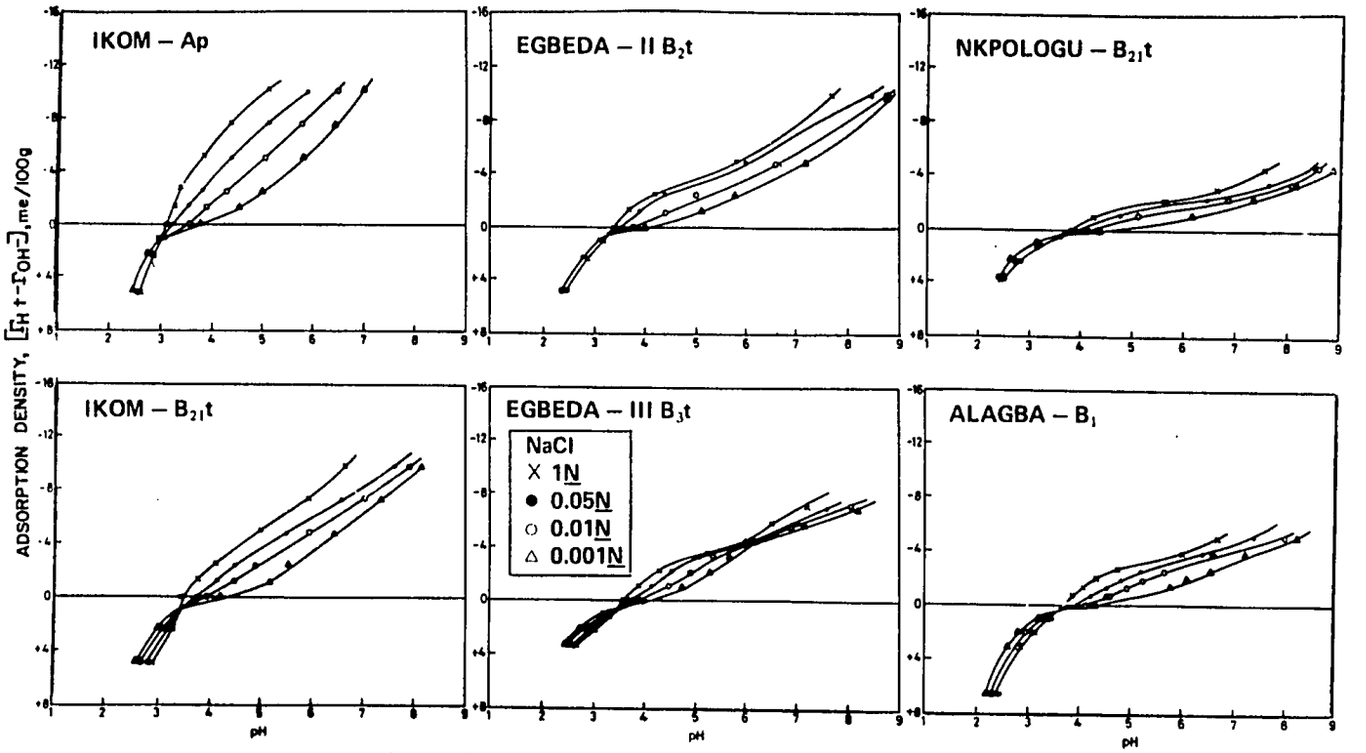

Fig. 1—Surface charge-pH curves of soils determined in NaCl.

with the negative delta pH values, ($pH_{KCl}-pH_{H2O}$), of the soils (Table 2). The PZC of the charge-pH curves was on the acid side of the zero point of titration (where equal quantities of HCl and NaOH were added). This has been attributed to the presence of permanent negative charge (van Raij and Peech, 1972).

The Ikom soil, derived from basalt, showed the largest pH-dependent charge. The surface charge of the gibbsite-containing Nkpologu soil, derived from Cretaceous sandstones, was the least pH-dependent and the Egbeda soil, derived from Pre-Cambrian basement complex rocks, showed intermediate values. The varying amounts of pH-dependent charges is probably related to the physicochemical state of the oxide minerals in the soil since the specific surface area and the total free iron oxide content of the three soils also follow the same trend (Table 2). The effect of organic matter, which tends to lower the PZC, was not as pronounced as that reported by van Raij and Peech (1972) and Keng and Uehara (1973) for Oxisols and Ultisols.

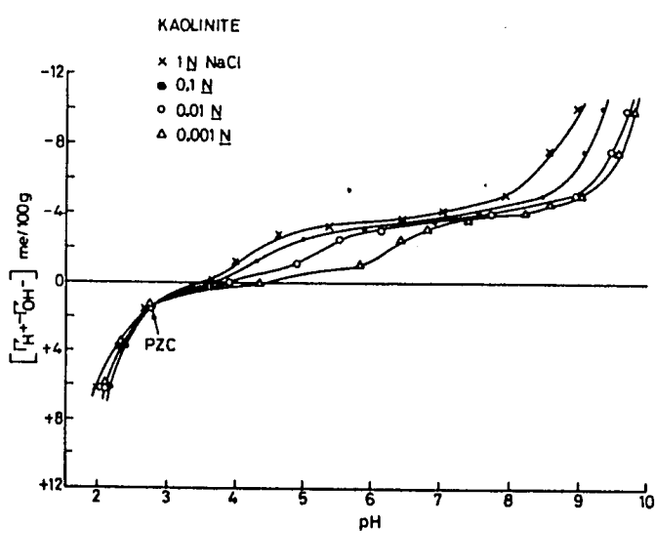

Fig. 2—Charge-pH curves of kaolinite.

The IIIB3t horizon of the Egbeda soil gave a peculiar type of charge-pH curve showing a second inflection point near pH 6.5 in addition to the PZC which occurred at pH 3.5 (Fig. 1). The effect of electrolyte diminished at the second inflection point, but the charge curves did not cross one another. These curves are similar to those of a kaolinite sample obtained from Wards Natural Science Co. (Fig. 2) indicating that the kaolinite in the IIIB3t horizon is of recent formation and that interactions with the edge surface of the kaolinite and Fe oxides have not yet taken place. In contrast, charge curves of the IIB2t horizon of the same profile showed strong association of Fe oxides with the edge surface of kaolinite as indicated by the disappearance of the second inflection point of the titration curves (Fordham, 1973).

The pH-charge curves of kaolinite showed two regions of the pH-dependent negative charge. The first region occurring between PZC (pH 2.8) and pH 7 may be attributed to the presence of exchangeable Al^{3+} on the charge sites of the "H-clay." The inflection point at near pH 7 is the isoelectric point of the edge surface (Rand and Melton 1975). The second region of the pH-dependent negative charge occurring above pH 8 is due to dissociation of the Si–OH groups.

The relatively low PZC values of the soils may be attributed to the large amounts of kaolinite and SiO_2 present in the soil in addition to the effect of organic matter. The PZC of kaolinite and SiO_2 occurs at pH 3.5 and 2 respectively (Parks 1967) while that for synthetic hematite and goethite occurs between pH 7-9 (Parks and de Bruyn, 1962; Atkin-

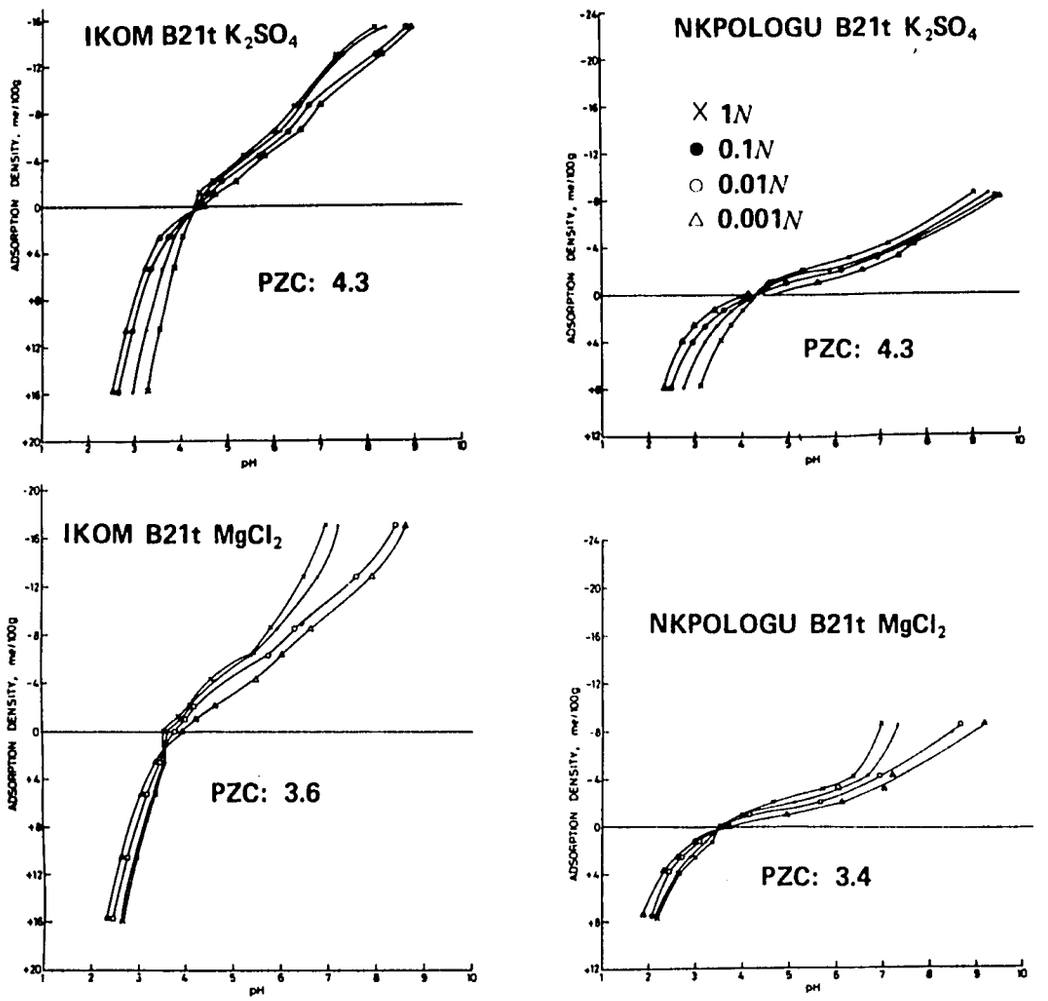

Fig. 3—Charge-pH curves of Ikom and Nkpologu soils determined in K_2SO_4 and $MgCl_2$.

son et al., 1967; Breeuwsma and Lyklema, 1973). Parks (1967) also showed a near linear variation of PZC with varying composition of Fe_2O_3 and SiO_2 in a complex oxide system. Moreover, the presence of small amounts of specifically adsorbed Si, Mg, and Ca on Fe oxides may also contribute to the low PZC of the soils used in this study.

The charge-pH curves for the B_{21t} horizon of the Nkpologu and Ikom soils in K_2SO_4 and $MgCl_2$ at four salt concentrations ranging from 0.001*N* to 1.0*N* clearly intersected one another (Fig. 3) The PZC values of the Nkpologu soil are 3.4 in $MgCl_2$ and 4.3 in K_2SO_4. PZC values for the Ikom sample are 3.6 in $MgCl_2$ and 4.3 in K_2SO_4. In all cases, the PZC values were on the acid side of the zero point of titration. The shift of the PZC to a higher pH value in the presence of K_2SO_4 in both soils as compared with the PZC measured in NaCl (Fig. 4) clearly indicates the specific adsorption of sulfate ion (Breeuwsma and Lyklema, 1973). There is also a considerable increase in the positive charges on the soil colloid surfaces in the presence of K_2SO_4 as compared with that in NaCl and $MgCl_2$. The surface charge characteristics due to the presence of sulfate are in agreement with that reported for synthetic hematite (Breeusma and Lyklema, 1973) and for the Ultisol and Oxisol samples from Hawaii (Keng and Uehara, 1973).

No significant shift of PZC was observed in the presence of $MgCl_2$ as compared with that in NaCl even though the negative charge on the soil was increased considerably by the presence of Mg^{2+} ions in the system. The lack of a detectable shift in PZC by Mg^{2+} might be related to the fact that the presence of permanent negative charge has already resulted in a significant shift of the PZC of the soil below that of a pure oxide system. Therefore, specific adsorption of Mg is unable to cause any further detectable shift of the PZC to a lower value.

Cation and Anion Retention by Soils:

The magnitude of both positive and negative charges as measured by Na^+ and Cl^- retention as a function of pH and electrolyte concentration, is in good agreement with the charge-pH curves of the soils (Fig. 5 and 6). The Nkpologu soil bears little positive and negative charges within the pH range studied (pH 2.5 to 6.5). This confirms the low effective CEC value of the soil determined by the sum of exchangeable bases and KCl-extractable acidity as given in Table 2.

In contrast, the basaltic Ikom soil has an appreciable positive charge at its natural pH (pH 5.8), although the soil bears net negative charge (Fig.6). Eleven successive wash-

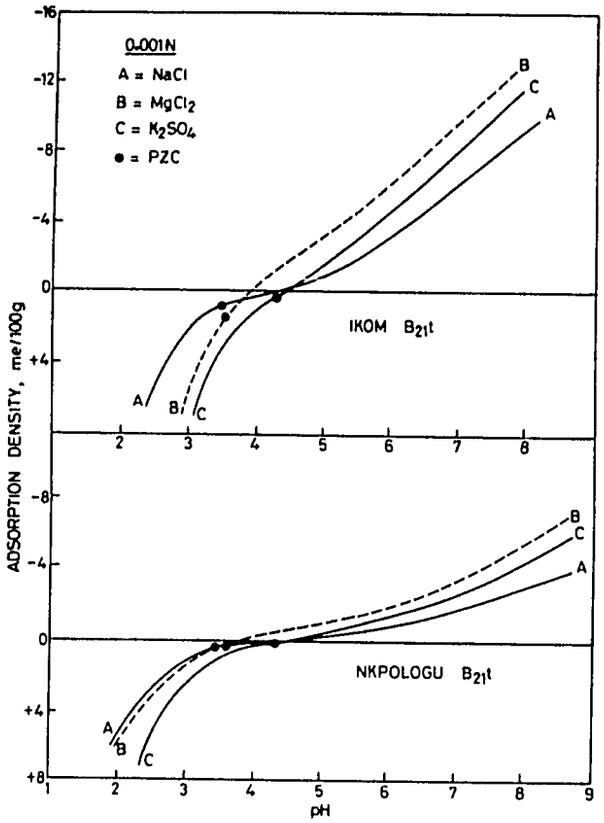

Fig. 4—Charge-pH curves of Ikom B21t determined in 0.001*N* NaCl, K_2SO_4 and $MgCl_2$.

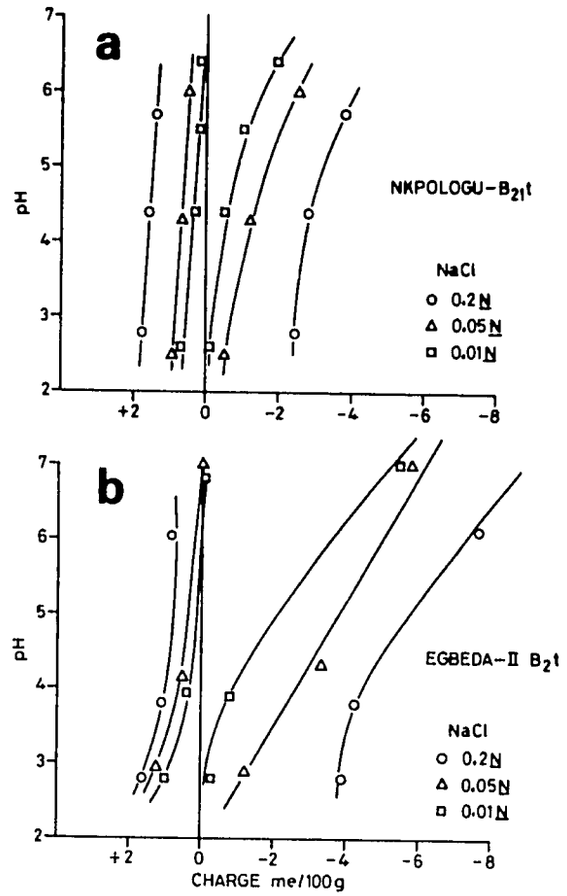

Fig. 5—Positive and negative charges of *(a)* Nkpologu B21t *(b)* Egbeda B2t, as determined by Na adsorption.

ings with dilute NaCl at lower pH (pH 2.5 to 5) as described by van Raij and Peech (1972) were not as effective in removing exchangeable Al ions from the Na system as were the 0.5*N* NH_4NO_3 extracts used to displace the adsorbed Na^+. The negative charges calculated by adding the Al^{3+} to the Na^+ value (Fig. 6) indicate the presence of permanent negative charge in the soil of approximately 4 meq/100 g with the negative charge in 0.01*N* NaCl almost independent of pH below 5.0. The Al ions apparently occupy nearly all the negative charges at near pH 3.0 in spite of the washing of the soil with 0.2*N* NaCl followed by successive equilibrations with 0.01*N* NaCl at the same pH condition; i.e. the Al^{3+} ions are apparently being held strongly at the permanent negative charge sites and the highly hydrated Na^+ in the dilute NaCl solution are unable to displace them from the clay surface.

Cations with lower degree of hydration such as Cs^+ or K^+, may be more effective than Na^+ in replacing adsorbed Al^{3+} during washing. It is therefore misleading when adsorbed Al^{3+} is not included as counter ions, since the negative charge determined by the adsorbed Na^+ alone indicates that the soil contains negligible amount of negative charge at pH 3. The Nkpologu and Egbeda soils also had signifi-

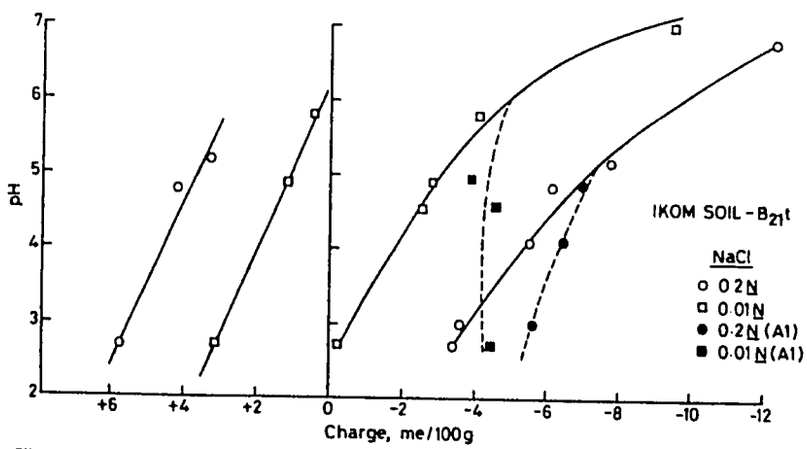

Fig. 6—Positive and negative charges of Ikom B21t determined by Na and Al adsorption.

cant quantities of exchangeable Al^{3+} (Table 4) although this is not shown in Fig. 5. These data indicate that the Egbeda and Nkpologu soils also contain a small amount of permanent negative charge.

The origin of the permanent negative charges is apparently due to structural substitutions in kaolinite and Fe oxides since the subsoil samples do not contain any detectable amount of 2:1 type layer silicates (Gallez et al., 1974). It has been reported that isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer of kaolinite and the structural substitution of Mg^{2+} and Li^{+} ions for Fe^{3+} in hematite and goethite will give rise to excessive permanent negative surface charge (Grim, 1968; Follet, 1965; Thomas and Swoboda, 1962).

Evidence has also been reported indicating the presence of a permanent positive charge in soils due to structural substitution of Ti^{4+} for Fe^{3+} in Fe oxides (Sumner and Davidtz, 1965). However, soils used in this study contain negligible amount of permanent positive charge as indicated by Cl^{-} adsorption from 0.01*N* NaCl solution (Fig. 5 and 6).

GENERAL DISCUSSION

Results shown here for Nigerian soils and those reported by van Raij and Peech (1972) and by Keng and Uehara (1973) for soils from Brazil and Hawaii confirm that the surface charge of Alfisols, Ultisols, and Oxisols in the tropics generally follow the constant potential model although they do contain some permanent negative charge. The PZC value of the subsoil samples (Bt horizon) measured in NaCl follows the order of Alfisols<Ultisols<Oxisols with average pH values of 3.5, 4.0, and 5.5, respectively. This sequence seems to reflect the degree of chemical weathering of the soils, particularly with regard to the degree of desilication and the surface characteristics of Fe and Al oxides in the soil (Herbillon, 1974). The PZC value measured in an indifferent electrolyte may thus be a useful criterion for soil taxonomy of tropical soils.

The dominance of constant potential type colloids in tropical soils indicates that different procedures should be used for cation and anion exchange capacity measurements. Since the magnitude and sign of surface charge varies with the nature and concentration of soluble salts in the solution phase, the CEC measured by saturating with *N* NH_4OAc at pH 7, and the "exchange acidity" measured by 0.5*N* $BaCl_2$ at pH 8 may be a gross over-estimation. Moreover, washing with alcohol-water mixture during the acetate displacement procedure results in a loss of absorbed cations and anions due to a decrease in electrolyte concentration and consequently, an expansion of the diffuse double layer (Sumner, 1963). Hence, during the neutral NH_4OAc displacement procedure the amount of negative charge of the soil is first raised due to high electrolyte concentration and high pH, but it is then reduced to some extent as a result of washing. A more realistic CEC measurement of these soil systems would be to determine the net electrical charge of the soil in a dilute electrolyte with concentration similar to that encountered in the soil solution (van Raij and Peech, 1972). This would involve the measurement of positive and negative charges using a procedure similar to that described by (Schofield, 1949). The Schofield procedure can be somewhat simplified by using X-ray fluorescence spectroscopy (Greenland, 1974) or radioisotopes to determine the concentration of adsorbed ions.

Table 4—Negative charge of soils measured by Na^{+} adsorption at pH 3 with and without correction for adsorbed Al^{3+}.

Soils	Effective CEC	Negative charge measurement			
		NaCl concn.	Na^{+} adsorbed	Al^{3+} adsorbed	$Na^{+} + Al^{3+}$
	meq/100 g	*N*	meq/100 g		
Egbeda IIB2t	4.7	0.01	0	4.1	4.1
		0.05	1.0	3.1	4.2
		0.2	3.0	1.2	4.2
Egbeda IIIB3t	3.9	0.01	0	3.3	3.3
		0.05	1.0	2.6	3.6
		0.2	2.5	1.0	3.5
Nkpologu B21t	1.8	0.01	0	1.3	1.3
		0.05	0.5	1.0	1.5
		0.2	2.0	0.3	2.3
Ikom B21t	4.4	0.01	0	5.7	5.7
		0.05	1.0	5.6	6.6
		0.2	3.0	3.3	6.3

An alternative procedure for routine CEC estimation would be to determine the sum of cations including exchangeable bases as measured by successive 1*N* NH_4OAc extraction and the exchange acidity (Al + H) as determined by 1*N* KCl extraction. The CEC determined in such a manner is called "effective CEC" (Kamprath, 1970). It should be more indicative of the actual CEC of soils in their natural condition although the amount of exchange acidity will depend on the initial pH of the KCl solution in relation to PZC; i.e. the soil will specifically adsorb or release H^{+} as well as release exchangeable H^{+} on KCl extraction. Results given in Table 4 and unpublished data from this laboratory on the effective CEC measurements of a large number of samples of West African soils showed close agreement with the net charge measurements in unbuffered dilute salt solutions.

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