ELECTRO-CHEMICAL PROPERTIES OF SELECTED OXISOLS AND ULTISOLS OF KERALA WITH SPECIAL REFERENCE TO CHARGE CHARACTERISTICS AND SURFACE MINERALOGY

By

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THESIS

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DECLARATION

I hereby declare that this thesis entitled "Electro-chemical properties of selected Oxisols and Ultisols of Kerala with special reference to charge characteristics and surface Mineralogy" is a bonafide record of reserach work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title of any other University or Society.

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CERTIFICATE

*Certified that this thesis entitled "Electro-chemical properties of selected Oxisols and Ultisols of Kerala with special reference to charge characteristics and surface Mineralogy" is a record of research work done independently by Mr. **P. Rajendran** under my guidance and supervision and that it has not previously formed the basis for the award of any degree, fellowship or associateship to him.*

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INTRODUCTION

INTRODUCTION

World population, currently estimated at more than 4.5 billion, has increased at a rate of 2% per year during the last two decades. The outcome of the race between world food production and population will largely be determined in the tropics where most of the world's undernourished people live. During the last two decades food production increased at a slightly faster rate than population in food-deficient countries (Sanchez and Cochrane 1980). Increased food production in the future must come from intensification of agriculture especially in developing countries and /or from the expansion of frontiers to include new land mainly in the tropics. To meet this goal of increased food production, areas dominated by low activity clay soils (LAC) such as Oxisols and Ultisols of the tropics are to be brought under plough (NAS, 1977).

Oxisols are the most abundant soils in the humid tropics covering an estimated 35 % of the land area followed by Ultisols, the second most abundant with an estimated area of 28% of the land cover (Kang and Spain, 1984).

In India Oxisols and Ultisols are mainly distributed in Kerala , West coast of Konkan and Goa, East coast of Tamil Nadu, Orissa, parts of Himachal Pradesh, Bihar, Madhya Pradesh and Maharashtra (Varghese 1981).

These soil groups characterized by low activity clays with low cation exchange capacity are known to have serious physical and chemical constraints for development of efficient crop production systems (Sanchez and Salinas 1981).

The red and laterite soils of Kerala occupying nearly twothirds of the total geographical area, included under Oxisols and Ultisols offer very serious problems of management. Though considerable data has been accumulated on fertility studies in these soils, reported information on the electro-chemical properties of these soils are scanty and meagre.

The electro-chemical and mineralogical properties of these soils are totally different from the other major soil groups of the state. Clay minerals with the exception of more resistant kaolinite are scarce (Varghese 1981). Intense chemical weathering removes silica and bases from the soil profile during pedogenesis, leaving clay fractions containing high amounts of iron, aluminium and often manganese oxides, kaolinitic clay minerals and a small amount of organic matter. The influence of the mineralogical composition of similar soils on the electro- chemical properties is clearly shown by their behaviour which is markedly different from that of soils of the temperate regions or regions with thick forest cover (Van Raij and Peech, 1972).

Most of the peculiar properties of these soils are attributed to the existence of considerable amounts of positive electric charges and very low cation exchange capacity mainly due to iron and aluminium oxides (Gillman and Abel, 1987). Another important aspect is the extreme ease with which cations held by highly weathered soils are hydrolysed. It is now known that the density of both negative and positive charges in such soils is highly P^H dependent and research in soil chemistry in recent years has helped to dispel many earlier misconceptions (Juo and Adams, 1984). In soils of temperate regions however, a permanent negative charge predominate and the positive charge is small or non existent at least in the P^H range of natural soils. Thus approaches and methods developed to study the electro-chemical behaviour of such soils cannot be applied as such for the study of Oxisols and Ultisols.

Considering the extreme types of soil colloids, with permanent charge and P^H dependent charge, analogues are found in colloid chemistry. They are systems with either completely polarizable interfaces or completely reversible interfaces (Keng and Uehara 1974).

In general soils and especially clay minerals have been treated as completely polarizable systems or in other words, as systems with a permanent negative surface charge. At least two factors contributed to the swing towards the permanent charge concept. First, virtually all soil mineralogical research was conducted in Europe and North America. Researchers found ample evidence to show that the dominant soil minerals in the colloidal fractions were of the permanent charge type. The P^H dependent charge components such as amorphous coatings, iron aluminium oxides and hydrous oxides were treated as contaminants and largely ignored. Studies conducted by many workers (Van Raijand Peech 1972, Gillman and Uehara, 1980 and Gillman and Abel, 1987) have now proved that soils with variable charge colloids are similar to reversible interfaces and the surface charge depends on the electrolyte concentration as well as on the activity of potential determining ions in solution. At any given activity of the potential determining ions in solution, the electric potential at the surface is constant. Thus these soils can be treated as "constant potential" systems. In many instances the hydrogen ions (and the hydroxyl ions) can be considered as the potential determining ions.

The treatment of Kerala Oxisols and Ultisols as constant potential systems, although theoretically sound has not been attempted so far. Further the fundamental relationships among P^H, surface charge, electrical potential, electrolyte concentration and valence also are yet to be studied in these soils.

The purpose of this thesis was thus to study the electro-chemical properties of six selected Ultisols and one Oxisol representing the important pedological units having a wide geographical distribution in the state. An effort was made to rationalize the observed variation of positive and negative electrical charges under varied experimental conditions. The soils were treated as chiefly constant potential systems and the theory of the planar diffuse double-layer applicable to lower surface potential, was used to interpret some of the results.

With the above theoretical background in view, the following major objectives were set for the programme.

1. To evaluate the charge contributing factors and their inter-relationships.

2. To assess the zero point of charge (zpc) and the magnitude of charge in zpc due to variation in soil constituents.

3. To study the effect of P^H, nature and concentration of electrolytes on charge character.

4. Characterization of permanent and P^H dependant charges by various methods.

5. Evaluation of different methods of ion exchange measurements.

6. To study the contribution of organic matter and sesquioxides towards exchange properties.

7. To study the mineralogy and surface features of the clay colloids.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

The existence of both negative and positive charges on soil particles recognized long ago by many workers (Mattson, 1927, 1931; Schofield, 1939), is responsible for ion exchange properties, permitting them to act as reservoirs of chemical elements used by plants as nutrients. The most important fundamental phenomenon in nature next only to photosynthesis is thus justified by the part it plays in regulating the suite of cations and anions in the soil and their composition in the soil solution. The bulk of the work done in this direction however is in soils of the temperate regions (Wild, 1988). Temperate soils are rich in organic matter and clay minerals with very high negative charge density. The soils of the humid tropics and subtropics in contrast have low activity clays. These soils are chiefly kaolinitic Alfisols and the oxidic Oxisols and Ultisols (Juo and Adams, 1984). These impoverished though potentially arable soils contain predominantly kaolinite, Fe and Al oxides and hydrous oxides in the clay fraction. Thus the chemical properties of these soils are characterized by low effective CEC and low ionic strength in the soil solution.

The extent of area covered under similar soils in Kerala accounts to nearly two third of the total land area (Status Report. KAU, 1989).Although considerable literature has been generated on fertility investigations in these soils, a systematic work to study the charge behaviour has not been attempted so far. Investigations already conducted on different aspects of the Low Activity Clay (LAC) soils are classified and reviewed in this Chapter.

1. Theoretical Orientation to Ion Exchange in Soils

The excess surface charge that the solid matrix of the soil hold, that must be balanced by free ions of opposite charge, the so called counter ions, leads to the origin of ion exchange in soils. The excess surface charge in ion exchangers is established by an imbalance of electrical charge within the frame work or by proton transfer mechanisms (Raman, 1986).

With the advent of modern colloid chemistry, the double layer theory developed to describe phenomena occurring at electrically charged interfaces,by Gouy (1910, 1917) and independently by Chapman (1913) has been extended to soil systems also (Wiklander, 1964). An improvisation to the Gouy-Chapman scheme suggested by Stern (1924) has also been successfully adopted to explain the double layer concept of high surface potential soil systems .A brief description of the essence of the two theories have been attempted hereunder, as some of the derivations of the same have been used for calculations in the present study.

1-1 The Gouy-Chapman theory

This theory describes the distribution of counter- ions and co-ions in the liquid part near a solid-surface interface, by relating variables such as surface charge, electrical potential, concentration of ions and distance. To make things more familiar, simple and also to be consistent with much of the work done on soils and clays, negatively charged surfaces will be considered. However, the theory given will be equally valid for positively charged surfaces too, provided the correct signs are introduced (Van Raij and Peech, 1972; Wann and Uehara, 1978).

The model according to Gouy (1910, 1917) assumes negative point charges smeared out uniformly over a planar surface. The counter ions, also assumed to be point charges, are attracted to the surface by Coulomb forces while at the same time, they tend to diffuse away due to concentration gradient. The net result at equilibrium is a higher concentration of cations near the surface, diminishing with distance until the equilibrium concentration in the bulk of the solution is attained. The anions or co-ions, behave in the opposite manner, being repelled from the surface and increasing in concentration with distance. The distribution of ions in the diffuse layer is governed by the Boltzmann relation

$$ni = n \exp(-zie\psi/KT) \qquad \text{..........1 - (1)}$$

in which 'ni' is the concentration of ions of kind i, in number of ions per ml, n is the concentration of the equilibrium solution, zi is the valence of ions of kind i, e is the electronic charge, ψ is the electric potential and KT represents the average kinetic energy (figure 2).

The relation was further simplified as follows considering the negatively charged surface as being a plane and infinitely large.

$$d^2\psi/dx^2 = -\ 4\pi p/\varepsilon \qquad \text{...........1-(2)}$$

The electric potential varies from a certain value at the plane to zero in the bulk solution. 'x' is the distance from the plane, 'p' is the net volume charge density, and ε is the dielectric constant of the medium.

Considering that only symmetric electrolytes will be treated the net charge density is given by

$$P = ze(n^+ - n^-) \qquad \text{..........1 - (3)}$$

where n^+ and n^- stand for the concentrations of the cation and the anion, respectively. For distances far enough from the surface, $n^+ = n^- = n$. Making use of the mathematical identity $\sinh (X) = 1/2\, (e^X - e^{-X})$; equation (3) may be written as

$$P = -2nze \sin h \,(ze\psi/KT) \qquad \text{..........1 - (4)}$$

This equation is now substituted in the equation (2) for p and the fundamental equation of the double layer is obtained.

$$d^2\psi/dx^2 = (8\pi\, nze/\varepsilon) \sin h(ze\psi/KT) \qquad \text{..........1 - (5)}$$

The following defined quantities are introduced in the subsequent equations.

$$y = ze\psi/KT;\ yo = ze\,\psi 0/KT \qquad \text{..........1 - (6)}$$

$$k^2 = 8\pi\ ne^2z^2/\varepsilon KT \qquad \text{..........1 - (7)}$$

$\psi 0$ represents the surface potential. It is convenient to remember that at 25°C KT has the value of 25.7 electron milli-volts and that y and yo are dimensionless. 'k' is given in units of reciprocal length and has the same significance as that in Debye-Huckel theory.

Equation (5) can now be rewritten as

$$d^2y/dx^2 = k^2 \sin h\, y \qquad \text{..........1 - (8)}$$

This equation can be integrated considering the boundary conditions that for $x = \alpha$, $y = 0$ and $dy/dx = 0$. The result is

$$dy/dx = 2k \sin h\,(y/2) \qquad \text{..........1 - (9)}$$

The electroneutrality of the system demands the surface charge to be balanced by the excess charge in the liquid phase.

$$\sigma = -\int_0^\alpha p\,dx \qquad \text{.........1 - (10)}$$

where σ, the surface net charge, is oppositely equal to the total space charge in the solution. The combination of equation (2) with (10) yields

$$\sigma = (\varepsilon/4\pi)\int_0^\alpha (d^2\psi/dx^2)dx = -(\varepsilon/4\pi)\,(d\,\psi/dx)\ X = 0$$

which by the insertion of equation (9) becomes

$$\sigma = (2n\varepsilon KT/\pi)^{1/2} \sin h \ (yo/2) \qquad \text{..........1 - (11)}$$

This is an important equation. The surface charge can be calculated from the surface potential at any concentration of the equilibrium solution.

The significance of 'k' is given by equation (7) and is proportional to the valence of the counter-ion and to the square root of the concentration of that ion in the solution. Qualitatively this means that an increase in the charge of the counter ion and/or increase in the concentration of the solution, will reduce the thickness of the double layer.

1-2 TheStern's treatment of the double layer

Stern (1924) introduced corrections in the double layer theory, one of which takes into account the finite size of the ions. According to Stern (1924) the ions cannot approach the surface beyond a certain distance. From this point to the plane, the potential varies linearly and the layer, called the Stern layer, is considered as a molecular condenser. Outside the Stern layer, the distribution of ions and the decay of the potential with distance from the plane, obeys the Gouy-Chapman theory outlined earlier. The structure of the double layer according to Stern defines $\psi\delta$, the potential at the limit between the Stern and diffuse layer (fig. 3), δ the thickness of the Stern layer.

The total surface charge here is balanced by the sum of the charge in the Stern layer σ 1, and the charge in the diffuse layer, σ 2.

$$\sigma = \sigma 1 + \sigma 2 \qquad \text{............. 1 – (12)}$$

Overbeek (1952) and Peech et al. (1953) have derived an equation for σ 1, considering the number of available sites on the surface for c$\overset{u}{\wedge}$nter ions in the Stern layer and in solution.

The charge of the Stern layer is thus given by

$$\sigma 1 = \frac{N_1 ze}{1 + (N_A P/Mn) \exp [- (ze \ \delta + \phi)/KT]} \qquad \text{..........1 - (13)}$$

In this equation N_1 is the number of adsorption spots available in 1 cm^2 of surface, N_A is the number of Avogadro, P is the density of the liquid, M is the molecular weight of the liquid, and ϕ is a chemical potential term introduced to account for additional forces acting on the counter ions.

The charge of the diffuse layer is given by the equation

$$\sigma 2 = (2n\varepsilon KT/\pi)^{1/2} \sin h\,(y\delta/2) \qquad \text{.........1 - (14)}$$

The charge on the surface is also given by the expression

$$\sigma = (\varepsilon'/4\pi\delta)\,(\psi o - \psi\delta) \qquad \text{..........1- (15)}$$

where 'ε'' is the dielectric constant in the stern layer.

With the above equations (12,13,14 and 15) it is possible to calculate the surface charge if the surface potential is known or vice-versa.

1-3 Types of double layers in soils

Considering the potential and the charge at the surface of colloidal particles as the master variables, two extreme types of double layer systems are recognized, depending on whether the charge or the surface potential remains constant upon changing the electrolyte concentration (Harkins, 1952).

According Van Raij and Peech (1972) this is true in the case of soils in which permanent and p^H dependant charges are recognized. He has thus described the following two types of electrical double layers on the basis of the mechanism by which free charges are distributed across a solid-solution interface.

(a) a reversible double layer which exists on the surface bearing a constant potential or variable charge and

(b) a completely polarizable double layer which exists on the surface bearing a constant charge.

Similar findings for weathered tropical soils have been reported by many workers (Parks and De Bruyn, 1962 ; Keng and Uehara, 1974 ; Gallez et al. , 1976 ; Laverdiere and Weaver, 1977 ; Gillman and Uehara, 1980 and Gillman and Abel, 1987).

1-3.1 Variable charge systems

This refers to the constant surface potential system as per reports of Van Raij and Peech (1972). The electric potential at the surface is determined by the activity of the potential determining ions in solution and by changing the indifferent electrolyte concentration, the surface charge should change, provided no alteration in the activity of the potential determining ions in solution is introduced (Parks and De Bruyn, 1962). In soils, most colloid systems have H^+ and OH^- as potential determining ions. Aluminium and iron oxides are good examples (Herbillon, 1988).

When a potential determining ion passes from solution to the solid surface it carries a charge with it. If the ionogenic group of an oxide surface is represented by $\underline{R}$-OH and assuming the surface to be in contact with sodium chloride solution, the following equations represent schematically, the build up of negative or positive surface charge, if H^+ and OH^- are the potential determining ions (Van Raij and Peech, 1972).

$$\underline{R}OH + NaOH \text{ ----> } \underline{R}\bar{O} \ldots\ldots Na^+ + H_2O \qquad \ldots\ldots\ldots 1 - (16)$$

$$\underline{R}OH + HCl \text{ ---> } \underline{R}OH^+{}_2 \ldots\ldots Cl^- \qquad \ldots\ldots\ldots 1 - (17)$$

Accordingly a positive charge originate due to adsorption of a proton while a negative charge is the result from the dissociation of a surface hydroxyl. The authors attributed this to the amphoteric behaviour of $\underline{R}$-OH. Iron and aluminium oxides are some of the several metal oxides that exhibit this property.

In an uncharged surface assuming H^+ and OH^- as the only source of surface charge, the build up of charge due to the adsorption of these ions

$$\sigma = e\,[\Gamma H^+ - \Gamma OH^-] \qquad \ldots\ldots\ldots\ldots 1 - (18)$$

where σ is the surface charge, e is the charge of an electron, $[\Gamma H^+ - \Gamma OH^-]$ represents net adsorption. If an excess of H^+ ions are adsorbed, the surface charge will be positive, likewise, it will be negative if an excess of OH^- ions are adsorbed. For gibbsite as an example, Van Raij and Peech (1972) proposed, formation of charge on the surface schematically as follows assuming Al (III) in an octahedral co-ordination

$$\underline{Al_2}\, OH^+{}_2 \text{ <--- } H^+ + \underline{Al_2}\, OH + OH^- \text{ ---}\underline{\geq A}l_2\, O^- + H_2O \qquad \ldots\ldots\ldots\ldots 1 - (19)$$

when the underscored symbols refers to species forming part of the solid surface. Thus acid dissolution, producing negative surface sites, is equivalent to adsorption of OH^-, whereas basic dissolution, giving rise to positive surface sites, is equivalent to adsorption of H^+. The exact state of affairs will be determined by the p^H and the concentration of the electrolyte. It is customary to refer to the activities of the potential determining ions in calculating the surface potential of variable charge soils. This means that, the p^H of the solution should be considered if H^+ and OH^- are the potential determining ions (Morais et al. 1976; Laverdiere and Weaver, 1977 and Uehara and Gillman, 1980).

The p^H at which the net surface charge reduces to zero is a characteristic value for a reversible interface and is called the zero point of charge, represented by zpc. The zpc may be visualized as the state in which only the uncharged intermediate species of the above reaction exist.

When the ionogenic group is located on a crystal edge rather than on the surface of the mineral, the following represents the formation of electric charges on the exposed octahedral aluminium groups.

$$\underline{Al}OH^{0.5-} + H^+ \dashrightarrow \underline{Al}\,OH_2^{0.5+} \qquad ....1\text{-}(20)$$

Equal amounts of the above species would necessarily have to be present at the zpc. Similar reactions are possible for Fe (III) systems also in soils (Herbillon, 1988).

If the surface charge is assumed to originate only from the adsorption of H^+ and OH^-, the surface electric potential due to charges is determined by the p^H of the equilibrium solution and is given by a Nernst type relation.

$$\psi_0 = (RT/F) \ln [(H^+)/(H^+)\,zpc]$$

$$= 59\,(zpc - pH)\ mV\ at\ 25^{\circ}C \qquad ....1\text{-}(21)$$

Thus it should be possible to calculate the double layer potential at any pH if the zpc is known.

1-3.2 Constant surface Charge Systems

Equation (3) implies that if the surface charge is constant, the potential has to change upon variation in electrolyte concentration of the equilibrium solution (Van Raij and Peech, 1972). The charge as per the equation cannot if it is inherent within the structure of the surface. It represents the case of the totally polarizable double layer

(Overbeek, 1952) and is applicable chiefly to constant charge colloids of the 2:1 type of the temperate regions (Juo and Adams, 1984). However, most of the past applications of the double layer theory to soils, the systems have been considered as having a constant surface charge (Wild, 1988), due to virtually all soil mineralogical research being conducted in Europe and North America wherein the soils are dominated by permanent charge minerals.

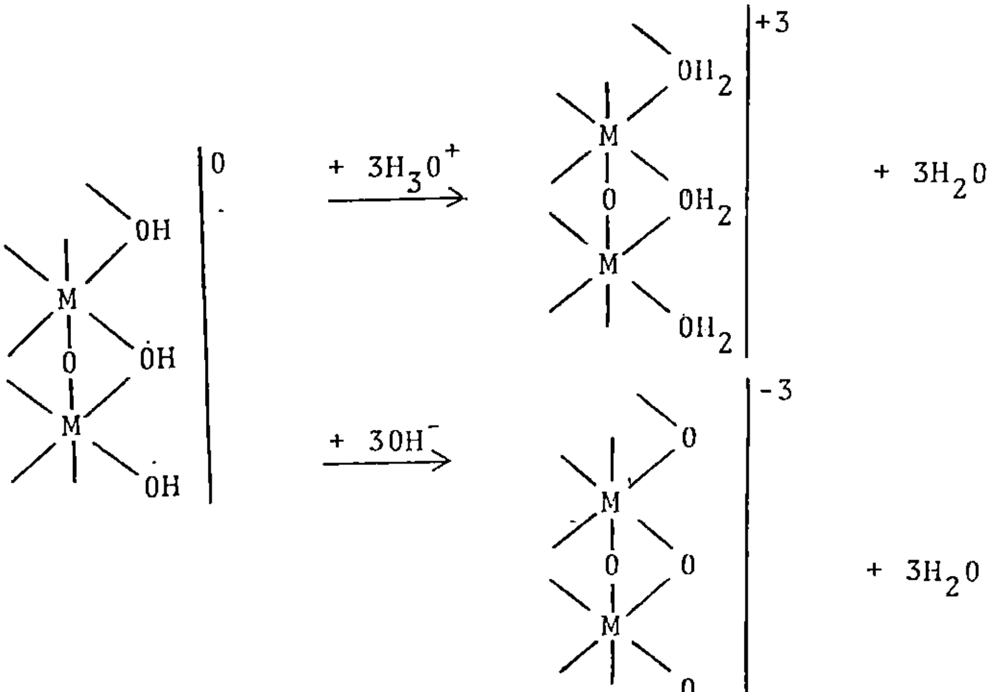
1-4 Exchange Properties of Soil materials in the Tropics

Clark et al. (1966) reported that the highly weathered soils of the tropics are characterized by an accumulation of iron and aluminium oxides. The finer fractions of these soils studied according to Van Raij and Peech (1972) contain organic matter, kaolinite, gibbsite and iron oxides as the major components. Studies by many workers (Keng and Uehara, 1974 ; Espinoza et al., 1975; Gallez et al. , 1976; Gillman and Abel, 1987) have confirmed that the charge properties of highly weathered soils of the humid tropics adhere closely to those exhibited by constant surface potential colloids.

1-4.1 Oxides

Many oxides according to Van Raij and Peech (1972) when in contact with electrolyte solutions, present reversible interfaces, thus behaving as constant potential type colloids. The chief components studied by them were iron and aluminium oxides, which usually dominate the clay fractions of tropical soils.

Studies conducted by many workers (Bolt, 1960 ; Parks and De Bruyn, 1962 and Yopps and Fuerstenau, 1964) proposed the following mechanism to explain the formation of charges in iron (III) and aluminium oxides.



Hingston et.al. (1967), Rajan (1976) and Gillman and Fox (1980) explained the charging phenomena to ligand exchange of oxyacids, anions like phosphate and silicate that can enter into six co-ordination with the aluminium or ferric ion on the crystal surface. The process of ligand exchange can be pictured as follows by a proportion of hydrogen ions being adsorbed by hydroxyls (Wild, 1988).

$$\left.\begin{array}{l|l} \text{Crystal} & OH_2^{+1/2} \\ & \\ \text{Surface} & OH^{-1/2} \end{array}\right|^{o} + H^+ + OH^- \text{---}\rangle \quad \left.\begin{array}{l|l} \text{Crystal} & OH^{-1/2} \\ & \\ \text{Surface} & OH^{-1/2} \end{array}\right|^{-1} + H^+ + H_2O$$

Thus these reactions explain the increase in cation exchange capacity of an oxide rich soil consequent to the addition of large doses of phosphates and silicates (Wann and Uehara, 1978).

Mechanism similar to the one given for aluminium and iron (III) have been proposed by many workers (Bolt, 1957; Parks and De Bruyn, 1962; Van Raij and Peech, 1972) to explain charge formation on silica surfaces. In highly weathered soils of the tropics removal of soluble silica to lower layers is appreciable and hence charge development by silica is of little significance.

De Bruyn and Agar (1962) pointed out that the existence of a zero-point charge on an oxide and the pH at which it is located, will depend on the relative basic and acidic properties of the solid. Strongly amphoteric oxides such as Fe_2O_3 and Al_2O_3 should have a zpc in the neighbourhood of p^H 7, while SiO_2 and acidic oxide, should be negatively charged even at low p^H values. Experimental values of zpc tend to support this statement though the variation is rather very wide (Parfitt, 1980 ; Stumm and Morgan, 1981). The reported values (Juo and Adams, 1984) are 9.5 for gibbsite, 8.1 for goethite, 7.5 for hematite, 6.9 for ferrihydrite and 9 for poorly characterized amorphous iron hydroxides.

Study conducted by many workers have (Sumner, 1963; Sumner and Davidtz, 1965 ; Sumner and Reeve, 1966) shown that the Fe and Al oxides in soils are usually responsible for the existence of positive charges and for the blocking of negative charges. However, above the zpc, oxides develop a negative charge and near the zpc both cation and anion retention is expected. (Zhabrova and Egorov, 1961).

1-4.2 Clay minerals

The most important clay mineral found in tropical soils is kaolinite which possesses a small cation exchange capacity and show a positive charge (Van Raij and Peech, 1972 ; Gallez et al., 1976 ; Morais et al., 1976 ; Grove et al., 1982; Wild, 1988 and Singh et al.,1991).

According to Parks (1967) the zpc values for Kaolinite predicted based on AlOH and SiOH sites were found to be 5.5 (hydrous) and 4.8 (anhydrous) both higher than the experimental values which varied from 3.3. to 4.9. The reasons for the discrepancy was attributed to the negative structural charge existing in these minerals, which tend to decrease the zpc to lower p^H values. Van Olphen (1963) and Parks (1967) reported that the low dissociation constant of SiOH groups and the higher dissociation constant of Al-OH groups occurring at the mineral surface and surfaces of Fe and Al oxides are chiefly responsible for the variation in the zpc of these components.

Follet (1965), Schofield (1954) and Van Olphen (1963), in separate studies suggested that the adsorption of small amounts of aluminium ions reverses the charge on the edges of silicate minerals to positive although silica surfaces normally carry a negative charge.

The separation of the negative charge into permanent and p^H dependant was first suggested by Schofield (1939) and the idea was later accepted by many (Van Raij and Peech, 1972 ; Uehara and Gillman, 1980 and Gillman and Abel, 1987) for the characterization of negative charges in soils and clays. According to the above authors kaolinite presents both type of charges, the permanent probably being the less important at high pH and pH dependant, most operational over a range of pH.

1-4.3 Organic fraction and other materials.

Studies by Overbeek and Jong(1949) showed that contribution of organic matter to charge properties of soils are predominantly pH dependant and controlled by proteins, the chief among the macromolecules, which present a net negative or positive or isoelectric charge. In contrast to this many workers reported (Broadbent and Bradford, 1952; Marshall, 1964; Wiklander, 1964; Coleman and Thomas, 1967) that the organic matter is predominantly acid in nature, with the acidic properties being determined mostly by carboxyl groups below pH 7 and the phenolic and enolic OH⁻ at higher pH values. Thus organic matter in soils never becomes isoelectric. This observation is in agreement with many recent reports (Uehara and Gillman 1981; Juo and Adams, 1984 and Wild, 1988).

Van Raij (1969) in a study of the Brazilian soils reported that the average contribution of organic matter to exchange properties of the soils was 74 per cent in the surace soil and 35 per cent for subsoils. Thompson et al. (1989) in a study of 4 soils of Iowa found that on an average organic matter was calculated to contribute 49 per cent of CEC and 19 cent of the surface area.

Among the remaining materials that occur in the clay fraction of soils and exhibit ion exchange properties, allophanes are the most important. They are amorphous alumino silicates with high surface area and high ion retention capacity for both cations and anions (Bolt, 1957; Wada and Ataka, 1958; Mitchell et al. 1964; Herbillon et al. 1976 and Herbillon, 1980).

2. Surface Charge Properties of Variable Charge Soils

2-1. Zero-point of charge

Zero point of charge (zpc) according to Parks(1967) and Gillman and Uehara (1980) is the pH value of soil solution at which the net surface charge on the soil particles resulting from the adsorption of potential determing ions H^+ and OH^- is zero. At this pH the absorption of H^+ and OH^- are equal and it is the point of intersection of potentiometric titration curves at different electrolyte concentration. This pH value refers to the point where there is an equal number of protonated and deprotonated sites on the variable charge surfaces in the soil.

Van Raij andPeech (1972) in a study of the electro-chemical properties of some Oxisols and Ultisols of Brazil has determined the zpc by potentiometric titration as a function of pH and electrolyte concentration. The values varied from 2.1 to 6.16. The electro-chemical behaviour of these soils was found to be similar to that exihibited by many metallic oxides. The estimated values of zpc increased with depth. The authors attributed the presence of large amounts of Fe and Al oxides for the higher zpc of the subsoils, while the presence of clay minerals with permanent negative charge as well as organic matter to the shift in zpc to lower pH values of surface samples.

Many workers have reported similar results (Gillman and Uehara, 1980; Gallez et al., 1976; Laverdiere and Weaver, 1977; Morais et al. 1976; Wada and Okamura,1983; Gillman and Sumner, 1987; Dolui et al., 1987;Gillman and Abel, 1987 and Misra et al., 1989).

Zpc according to the above authors reflect the overall mineralogical composition and organic matter content of the soil. The degree of chemical weathering particularly the degree of desilication also is indicated in the zpc as highly leached ferruginuos soils low in organic matter generally showed higher zpc values (Raman, 1986). Gallez et al. (1976) thus suggested the usefulness of zpc determinations as a criterion for soil taxonomy of tropical soils.

2-1.1 Determination of the zero-point of charge

Some of the important methods used include electro-kinetic methods, such as electro-osmosis, electrophoresis, and determination of streaming potentials, and other indirect techniques such as ageing of interfaces and the measurement of the release of the potential determining ions, extrapolation of the suspension effect to zero, and measurement of adsorption of potential determining ions by potentiometric titrations (Overbeek, 1952). Many workers have (Van Raij and Peech, 1972; Yopps and Fuerstenau, 1964; Uehara and Gillman, 1980) suggested the direct measurement of adsorption of potential determining ions by potentiometric titations as the best method for zpc determination. It also permits the estimation of the values of net charge on the surface, at different ionic strength and pH values.

2-2 Effect of pH and Electrolyte Concentration

The dependence of surface charge and surface potential on pH, electrolyte concentration and the dielectric constant of the solvent is implied in the modified Gouy-Chapman equation (Uehara and Gillman, 1980).

$$\sigma 0 = (2n\, \varepsilon\, KT/\pi)^{1/2} \mathrm{Sin\,h}\, z\, (1.15)\, (p^{H}0 - p^{H}) \qquad ....2 - (1)$$

where ε = dielectric constant of the solvent
$p^{H}o$ = zero point of charge, n = electrolyte concentration
K = Boltzmann constant. T = absolute temperature
z = counter ion valence.

Van Raij and Peech (1972) reported that upon decreasing the electrolyte concentration of the soil solution, magnitude of both the positive and negative charge decreased in some of the Oxisols and Alfisols of Brazil studied. At a particular concentration of the electrolyte a decrease in pH considerably reduced the CEC and increased the AEC. The same authors reported that the positive and negative charges of soils determined by the adsorption of divalent ions were higher than those obtained with monovalent ions, and even more so where both the cations and the anions are divalent in the electrolytes used.

Thus any attempt to change the concentration of the electrolyte and pH will change the surface charges measured, the hidden faults of buffered electrolytes of high concentrations used to estimate the CEC, like N NH_4 OAc ($p^{H}7$) is indicated here (Morais et al., 1976; Grove et al., 1982).

2-3 Methods of charge characterization

An unambiguous knowledge of soil charge characteristics and exchangeable ion suite under field conditions is a pre-requisite for effective soil fertility management of low activity clay soils. This knowledge is often difficult to obtain in view of the plethora of methods for determining soil exchange properties and rather wide range of opinion regarding interpretation of the data from those methods.

2-3.1 Problems in the determination of exchange capacity

The CEC and AEC of soils is difficult to determine in cases where part or the whole exchange capacity is pH dependant, because the final results depends strongly on the experimental conditions particularly pH, concentration and nature of index cations and anions used and the strength of the buffer solution (Van Raij and Peech, 1972). Failure to recognise this important point, according to Grove et al. (1982) is one of the main reasons for the confusion that now exists regarding the best method for determining the exchange capacities of tropical soils.

The use of N NH_4OAc (pH 7) for exchange capacity determinations in low activity clay soils have been questioned by many workers (Gallez et al., 1976; Grove et al., 1982; Juo and Adams, 1984 and Wild, 1988). Five parameters of equation 2-(1) are altered by the NH_4OAc method. These according to Uehara are dielectric constant (alcohol washing), salt concentration (varies from 1 N to near zero during washing), counter ion valence (use of monovalent NH_4^+ when dominant soil counter ions are divalent), zero point of charge (affected by acetate ion) and pH (buffered at pH 7). Thus exchange capacity determinations with NH_4OAc (pH 7) are gross over estimations. When unbuffered electrolytes are used in place of neutral NH_4OAc the problems are much corrected (Grove et al., 1982). Further the anion exchange capacity of the variable charge soils are conveniently ignored in most ion exchange determinations. Thus any method which can include AEC determination also along with CEC is considered ideal for such soils (Gillman and Sumpter, 1986).

2-3.2 New methods suggested for LAC soils

According to Van Raij and Peech (1972) determination of electrical charges cannot be done in highly weathered soils by a conventional method with a buffered electrolyte.

2-3.2.1 Schofield's method

Wild (1988) expressed the view that any method used requires definition of the experimental conditions with respect to the five parameters included in equation 2..(1) which affect the electrical charges measured. In this context many workers (Van Raij and Peech, 1972; Morais et al., 1976; Gillman, 1979 and Grove et al., 1982) have suggested the use of unbuffered electrolytes with a concentration similar to that encountered in the soil solution.

All the above methods are modifications of the method suggested by Schofield (1949) with 0.2 N NH_4Cl, adjusting the pH to desired values.

Van Raij and Peech (1972) used a modification of the above method with 0.2 N NaCl as the electrolyte for the estimation of CEC and AEC of 7 samples of Oxisols and Alfisols of Brazil. The pH of the samples was adjusted to four ranges and estimations were made. The result showed increase in negative charge with pH and a decrease in the positive charge with increase in pH. The net charge obtained was compared with the predicted values calculated as per theory and was found to be in good agreement.

2-3.2.2 Compulsive Exchange Method.

Gillman (1979) proposed a new method for the measurement of exchange properties of highly weathered soils. He modified the compulsive exchange method of Bascomb (1964) to allow the determination of cation exchange capacity and anion exchange capacity of soils. The soils wereequilibrated with unbuffered barium chloride solution, ultimately to get an ionic strength approximating that of the soil solution, so that the conditions under which determinations made are similar to those found in the field. The results obtained by this method was compared with other commonly used procedures and found more reliable and time saving. This method has been further modified and reported by Gillman and Sumpter (1986) to achieve greater simplicity.

2-3.2.3 Total cation exchange capacity(CECT), Basic cation exchange capacity (CECB) and Anion exchange capacity (AEC)

Gillman and Sumpter (1986), Gillman and Sinclair (1987) and Gillman and Abel (1987) proposed another method using 0.002 M $CaCl_2$ for the combined estimation of CEC and AEC. They used the term CEC_T, the total cation exchange capacity measured as the amount of Ca^{2+} + Al^{3+} adsorbed at a particular pH in 0.002 M $CaCl_2$ solution. Similarly CEC_B was used to designate the basic cation exchange capacity, the amount of Ca^{2+} adsorbed at a particular pH in 0.002 M $CaCl_2$ solution. The above authors observed high correlation between CEC_B at soil pH with compulsive exchange method and between CEC_T at soil pH with "effective CEC" measured as total exchangeable basis + normal KCl extractable aluminium.

2-3.2.4 The effective cation exchange capacity (ECEC).

The ECEC measured as the sum of the basic cations with exchangeable acidity determined by 1 N KCl (1:10) over a period of 2 hrs (Juo et al. 1976) gave high correlation with compulsive exchange CEC and CEC_B. As the basic cations were determined by a buffered electrolyte (NNH_4OAc; pH 7) the absolute values of ECEC was quite high and was not free from the blame of any buffered CEC estimation (Grove et al.1982). The ECEC is frequently being used for soil taxonomy purposes and is suggested as an improvement over N NH_4OAc; (pH 7) CEC (Soil Survey Staff USDA, 1990).

3. Specific surface determination.

Ion exchange cpacity of a soil is the product of the specific surface and the charge density. In most LAC soils the amount of permanent negative and positive charges are often small, cation and anion exchange capacity mostly arise from p^H dependant charge on the surface of oxide materials and organic matter. Thus the magnitude of CEC and AEC of a variable charge soil depends on its natural soil p^H relative to its zpc as well as specific surface area.

Juo and Adams (1984) reported that the specific surface of kaolinite and iron oxides and hydrous oxides, the chief inorganic constituents of LAC soils varies from 15-30 $m^2\ g^{-1}$ and 150-300 $m^2\ g^{-1}$ respectively. A significant portion of this iron hydrous oxides in the clay fraction may exist as surface coatings. Consequently, their specific surface is greatly reduced to 50-100 $m^2\ g^{-1}$.

Schofield (1947, 1949) used the negative adsorption data using the Gouy-chapman theory for the determination of specific surface. Gillman and Uehara (1980) effectively used this method for the calculation of the specific surface of the highly weathered Queensland soils. The calculated values were in good agreement with the measured values of the specific surface by other methods. The equation for estimating the specific surface S(cm^2/100 g) of a soil in a 1:1 electrolyte (Uehara and Gillman, 1980) is

$$\bar{\gamma} = \frac{q\,NS}{(z\beta N)^{1/2}} - \frac{4\,NS^2}{z\beta\,\gamma} \qquad \text{..........3 - (1)}$$

where γ, the total surface charge and $\bar{\gamma}$ the negative co-ion adsorption are in cmol (P^+) Kg^{-1} and N is the electrolyte concentration in cmol(P^+) ml^{-1}. If a 0.01 M 1:1 electrolyte is chosen for ion adsorption measurement the above equation becomes

$$\bar{\gamma} = 6.1 \times 10^{-9} S - \frac{3.774}{\gamma} \times 10^{-17} S^2 \qquad \text{..........3-(2)}$$

The specific surface of the variable charge soil component
$Sv = 1.83 \times 10^2 \; \gamma c^- \, m^2 \gamma^{-1}$
where γc^- is the negative adsorption of cations measured at two P^H units below P^H 0 in a 0.01 M 1:1 electrolyte.

Specific surface according to Gallez et al. (1976) could be estimated by a gravimetric method based on the retention of EGME or BET-N_2 adsorption by soil. The values obtained for some Alfisols and Ultisols from Nigeria varied from 18-222 m^2g^{-1} by the former method and from 3-63 m^2g^{-1} by the latter. Several workers have used these two methods for the estimation of surface area of soils and clays (Morais et al., 1976; Laverdiere and Weaver, 1977 and Van Raij and Peech, 1972).

4. Mineralogy of Low Activity Clay (LAC) Soils

Van Raij and Peech (1972) in a study of the electro-chemical properties of 7 Brazilian Alfisols and Oxisols reported the mineralogical composition. The ch~~e~~ief clay mineral identified was kaolinite with apreciable amounts of goethite, hematite and gibbsite. Gillman and Bell (1976) reported from a study of surface charge characteristics of six weathered soils of the Queensland the major clay mineral to be kaolinite with traces of chloritized vermiculite, illite,quartz and appreciable amounts of goethite, hematite and gibbsite. Studies on mineralogy of similar soils reported by many workers supported the above findings (Gallez et al., 1976., SCS. USDA, 1976., Grove et al., 1982 and Herbillon 1984).

5. Management of Low Activity Clay (LAC) Soils

Most of the under utilized, potentially arable but impoverished lands of the moist tropics are occupied by soils rich in variable charge minerals. The low nutrient retention capacity is in turn related to low specific surface, low surface charge density or a combination of both. Since the product of the specific surface and surface charge density is the cation-exchange capacity, the rejuvenation of impoverished, variable charge soils must involve increasing one or both surface parameters. Liming, incorporation of nitrogen rich green manures, minimum tillage, surface mulching, addition of phosphatic fertilizers, soluble silicates and organic matter are some of the physico-chemical methods suggested for the rejuvenation of these soils (Chen et al., 1973; Adams and Moore 1983 and Adams and Hathcock, 1984).

Kamprath (1984) reported that soils in which clay fraction is primarily low activity clays (Alfisols, Oxisols and Ultisols) in their natural state are acidic and infertile and can be made productive with liming and fertilization. He proposed the use of exchangeable Al as a criterion for calculating the lime requirement of variable charge soils. Crop growth in these soils according to the above author was less than 50 per cent of that of the limed soils when the exchangeable Al saturation was above 60 per cent. Another problem reported in LAC soils is the low amounts of native available 'p' coupled with high 'p' fixing capacity and very low levels of labile K (Graham and Fox, 1971 and Sharpley et al. 1984). Juo and Adams (1984) in a review of the work done in LAC soils reported that considerable amount of K applied to low CEC soils is readily leached when the CEC of the soil was less than 6 cmol (P^+) kg^{-1}. Frequent split application of fertilizers at low intensity coupled with crop rotation utilizing sub-soil K is suggested as a suitable proposition for such soils.

Many workers have reported the usefulness of the application of soluble phosphates, organic matter, and silicates in LAC soils to improve the CEC and for lowering the zpc. Economic constraints militate against using superphosphate solely for this purpose, but it is a significant by-product of such application. However, the use of low grade soluble silicates can be very easily recommended as it will improve the 'p' availability, replenish the soluble silica depletion in addition to the observed increase in CEC.

MATERIALS AND METHODS

Table 1. Location and classification of soils used for the study

Sl.No.	Location	District	Great group	Soil order	Longitude	Latitude
1.	Pilicode	Kasaragod	Kandiustult	Ultisol	75° 9' 55" E	12° 11' 53" N
2.	Pilathara	Cannur	Plinthustult	Ultisol	75° 13' 54" E	12° 05' 54" N
3.	Punalur	Kollam	Paleustult	Ultisol	76° 55' 00" E	09° 00' 00" N
4.	Arackal	Kollam	Kandiustult	Ultisol	76° 52' 30" E	08° 58' 00" N
5.	Karakulam	Thiruvananthapuram	Haplustult	Ultisol	76° 56' 55" E	08° 34' 16" N
6.	Maruthur	Thiruvananthapuram	Kandiustult	Ultisol	76° 58' 23" E	08° 32' 34" N
7.	Pachalloor	Thiruvananthapuram	Haplustox	Oxisol	76° 58' 06" E	08° 25' 16" N

MATERIALS AND METHODS

The programme of investigation planned may be grouped into the following experiments.

1. A laboratory study to assess the charge contributing factors and their inter-relationships in seven selected profiles of Oxisols and Ultisols representing the important pedological units with a wide geographical distribution in the state.

2. Preparation of potentiometric titration curves of selected horizons of the profiles to determine the zero point of charge (zpc) which reflects the electrochemical behaviour of constant potential systems.

3. A study of the effect of p^H, electrolyte concentration and type of index ions used on the measurement of surface charge in soils.

4.Propose a suitable method for the assessment of surface charge characteristics of soils, when both negative and positive charges are estimated in a simple manner, under conditions approximating those expected in the field. 5. Characterization of permanent and p^H dependant charges by direct ion adsorption and by theoretical methods.

6. Assess the contribution of organic matter and sesquioxides towards exchange properties of soil materials.

7. Study of (a) the mineralogy and surface features of fractionated soil components by XRDA and SEM methods and (b) the surface area of selected soil samples by different methods.

1. Study of charge contributing factors and their inter-relationships.

1.1 Collection of soil samples, location and classification.

A tentative classification of the seven soils used for the present study at the great group level, based on Soil Taxonomy, USDA (1978) is given in Table 1. The profiles were dug at each location (figure 1 and plates 1 to 7) as per prescribed procedures and collection of samples were made after demarcating the horizons. The profile features and field observations were recorded based on FAO guide lines (1978).

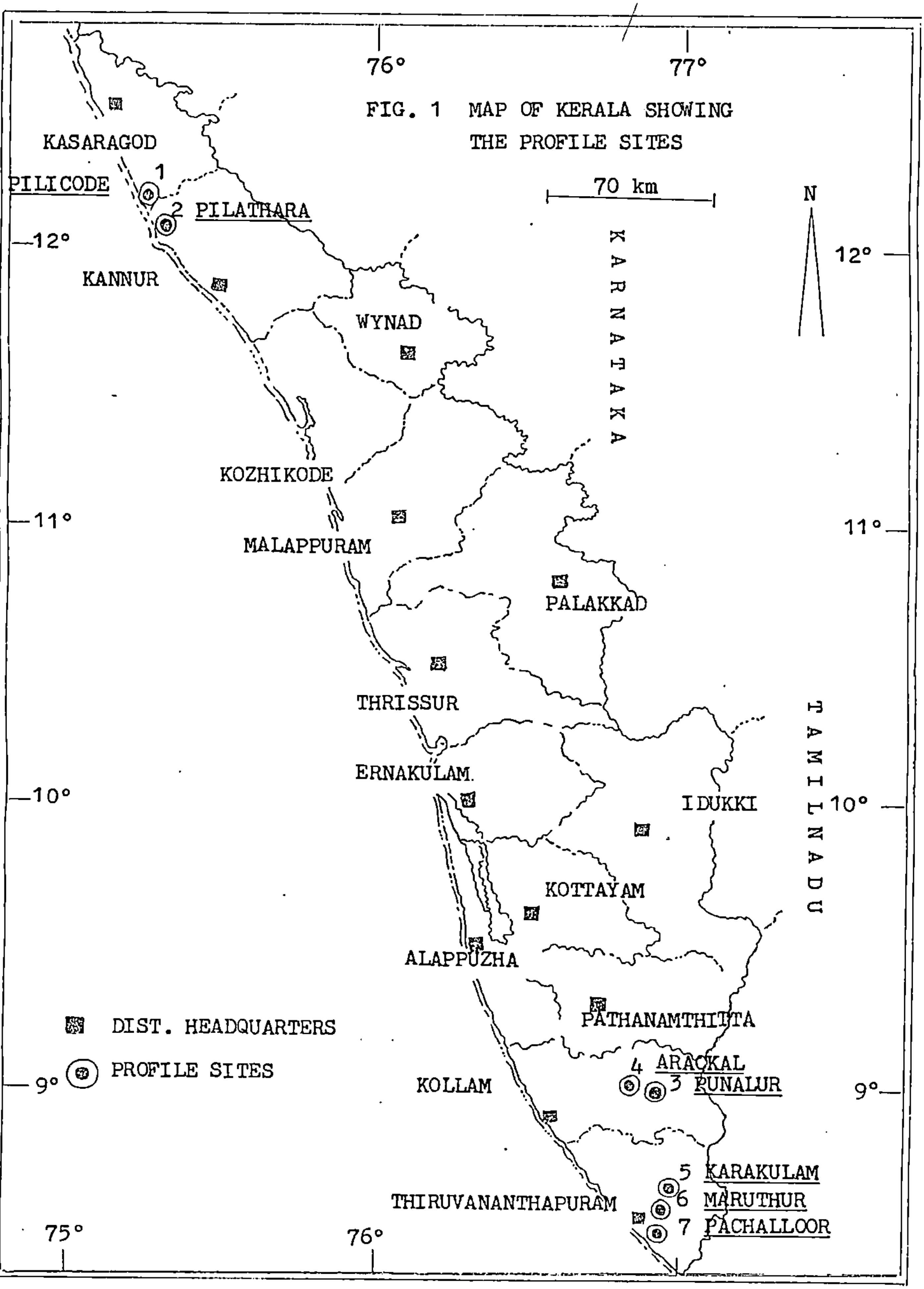


FIG. 1 MAP OF KERALA SHOWING THE PROFILE SITES

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Plate: I. Pedon. Kandiustult (Pilicode)

Plate: II. Pedon. Plinthustult (Pilathara)

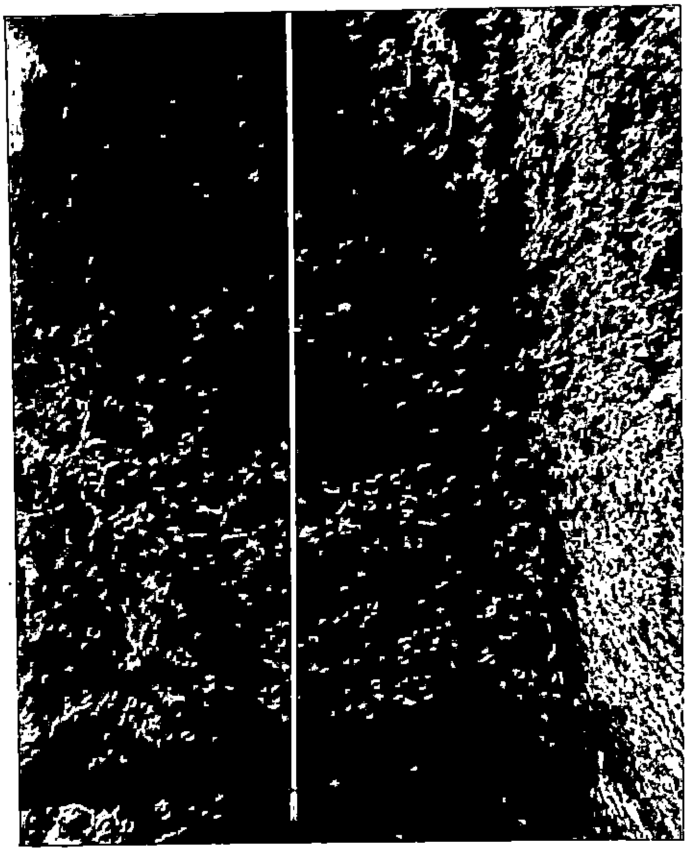

Plate: III. Pedon. Paleustult (Punalur)

Plate: IV. Pedon. Kandiustult (Arackal)

Plate: V. Pedon. Haplustult (Karakulam)

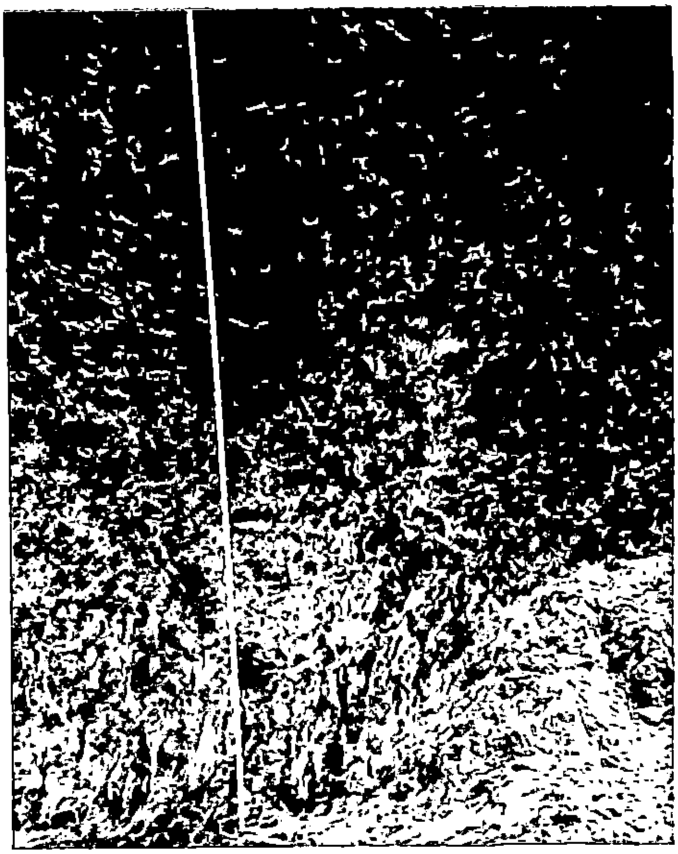

Plate: VI. Pedon. Kandiustult (Maruthur)

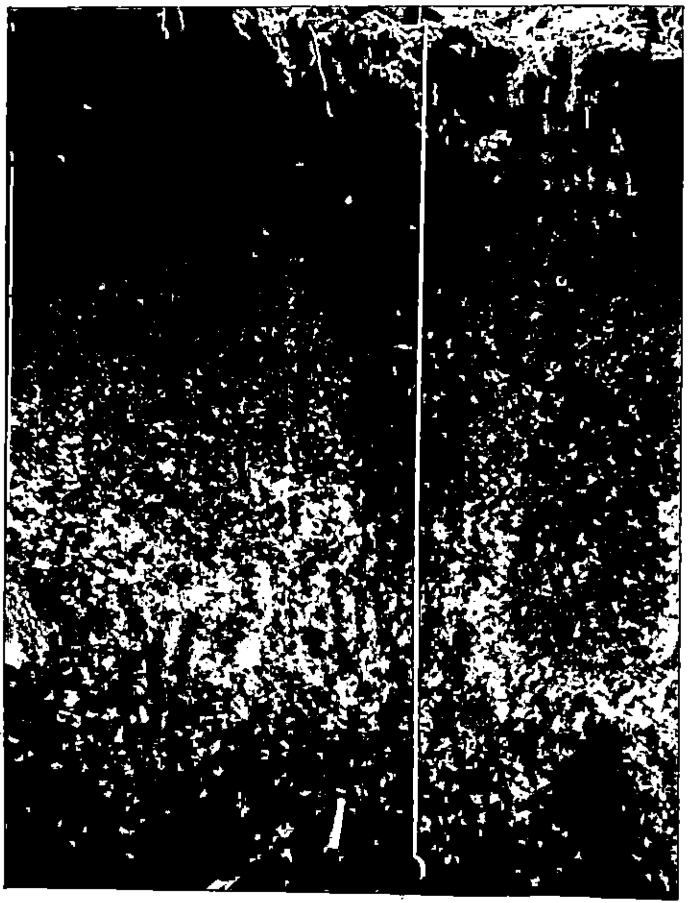

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Plate: VII. Pedon. Haplustox (Pachalloor)

1.2 Laboratory analysis

The bulk samples were air dried in shade. Gravel, plant roots and other debris were removed and the samples were gently powdered with a wooden mallet and passed through a 2mm sieve. The methods used for the important estimations made are outlined below.

Granulometric analysis of soils was carried out by the hydrometer method (Piper, 1942). The p^H of air dried samples from all the horizons was determined according to the method described by Peech et al. (1953) in water, 0.01 M $CaCl_2$, IN KCl and IN NaF. The glass electrode was immersed in the sediment and the Calomel electrode was immersed in the clear supernatant solution to avoid errors due to the liquid junction potential in the suspension. The solution to a soil ratio was 2.5:1 in KCl and $CaCl_2$ and 50:1 in NaF. p^H in water was measured in two ratios 1:1 and 2.5:1. Delta p^H was calculated by subtracting p^H water from p^H KCl (Mekaru and Uehara, 1972). The specific conductance was measured in the supernatant solution of a 1:1 soil-water suspension after the coarser particles had settled down. Organic carbon content was determined by the Walkley-Black method as described by Jackson (1958).

Exchangeable hydrogen and aluminium were estimated by extracting 10g soil with 100ml IN KCl under suction (Black, 1965). Total Fe_2O_3, Al_2O_3 and sesquioxides were determined as per standard analytical procedures outlined by Jackson (1958). Total Fe and Al were determined by the method described by Hesse (1971).

Fractionation of free oxides of iron and aluminium to estimate the contents of amorphous and crystalline forms was done following the method described by Mehra and Jackson (1960) modified by Kunze and Dixon (1986). Thus Fe_o, Fe_d, Al_o and Al_d were calculated from the data.

Neutral 1N ammonium acetate was used for the extraction of exchangeable bases (Jackson, 1958). After evaporation of the extract and oxidation of the organic matter with hydrogen peroxide Ca, Mg, K and Na were determined using an Atomic Absorption Spectrophotopmeter (Perkin-Elmer 3030). Cation exchange capacity was determined using 1N ammonium acetate and the adsorbed ammonium ions were distilled as described by Jackson (1958). Effective cation exchange capacity (ECEC) was calculated as the sum of all exchangeable cations (sum of exchangeable K, Na, Ca, Mg plus 1N KCl extractable Al) as proposed by USDA (1990). The anion exchange capacity of the samples was estimated by phosphate adsorption method as suggested by Hesse(1971).

1.3 Statistical analysis

Fifteen components consisting of charge contributing factors and parameters of charge assessment of the samples were subjected to correlation and path analysis to study the inter-relationships. All the samples collected from the different horizons of the profiles studied were included in correlation and path analysis.

2. Potentiometric titration curves

The potentiometric titration curves were prepared to determine the zpc and the distribution of the net electric charge with varying p^H and concentration of sodium chloride (indifferent electrolyte). The procedure suggested by Van Raij and Peech (1972) was followed. Fourteen samples representing the seven profiles, one each from the surface and sub-surface horizons, were used for the study. The details of the soils used were as follows.

(1) Kandiustult-Ap-Pilicode
(2) Kandiustult-B_2-Pilicode
(3) Plinthustult-Ap-Pilathara
(4) Plinthustult-B_2-Pilathara
(5) Paleustult-A1-Punalur
(6) Paleustult-Bt_2-Punalur
(7) Kandiustult-Ap-Arackal
(8) Kandiustult-B_2-Arackal
(9) Haplustult-Ap-Karakulam
(10) Haplustult-B_2-Karakulam
(11) Kandiustult-Ap-Maruthur
(12) Kandiustult-B_2-Maruthur
(13) Haplustox-Ap-Pachalloor
(14) Haplustox-B-Pachalloor

Serial titration curves were made using an individual sample for each point. To a 4 gram sample of soil in a 50ml beaker, appropriate amounts of NaCl, 0.1 N HCl or 0.1 N NaOH and water were added and the volume was made up to 20 ml. The final concentration of NaCl were 1.0, 0.1, 0.01 and 0.001 N. The beakers were kept in a closed humdified jar to prevent evaporation and were stirred occasionally. After 72 hours the p^H was measured by immersing the calomel electrode in the sediment as recommended by Peech (1953).

The amount of H^+ and OH^- adsorbed by the soil sample at any given p^H value, was taken as equal to the amount of HCl or NaOH added to the suspension minus the amount of acid or base required to bring the same volume and the same concentration of NaCl solution, without the soil sample to the same p^H. The zpc was considered to be the common intersection point of the titration curves carried out in the presence of four concentrations of NaCl. The net electric charge was calculated from the amount of H^+ and OH^- adsorbed with respect to the zpc.

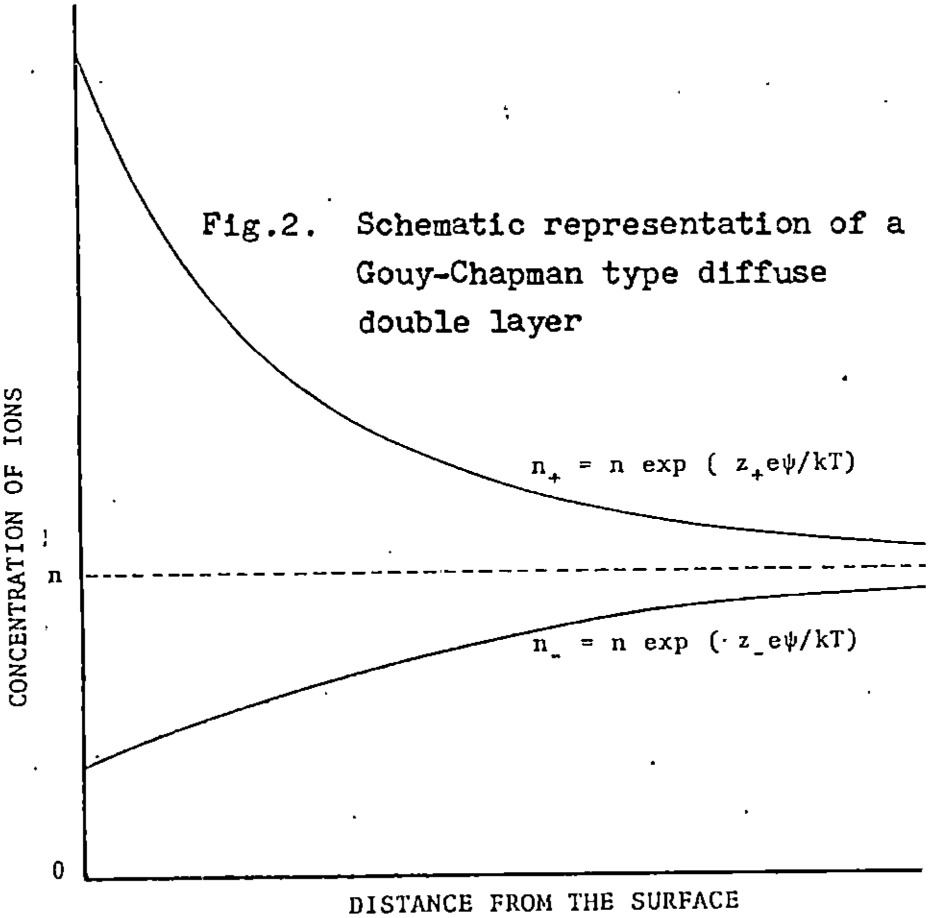


Fig.2. Schematic representation of a Gouy-Chapman type diffuse double layer

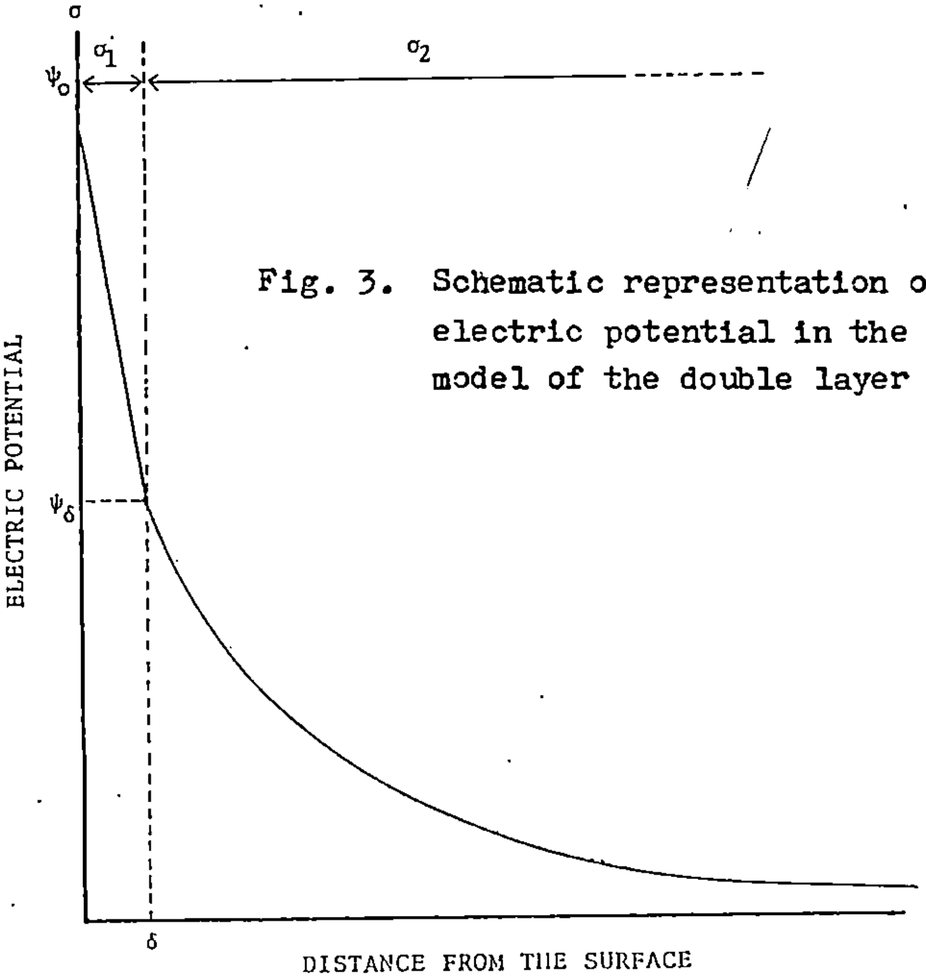


Fig. 3. Schematic representation of the electric potential in the Stern model of the double layer

3. Effect of p^H, salt concentration and nature of electrolytes on charge characteristics.

The A and B horizons of three Ultisols and one Oxisol were selected for this study. The samples included were Kandiustult -Ap and B_2 from Pilicode, Plinthustult-Ap and Bt_2 from Punalur and Haplustox-Ap and BA from Pachalloor.

Positive and negative charges of soils were determined by measuring the adsorption of both anions and cations from solutions of KCl and $CaCl_2$ as a function of P^H and salt concentration. The method used was similar to the one described by Morais et al.,(1976).

3.1 Determination of electric charges

Two grams of oven dry soil was placed in pre- weighed centrifuge tubes and 20 ml of the unbuffered electrolyte solutions was added. The P^H was adjusted to the desired value by the addition of HCl or NaOH. Four P^H values 3,5, 6 and 8 were fixed for the study. The next day the P^H was readjusted and the supernatant separated by centrifugation. Then the samples were washed five times with 0.2 N KCl, 0.1 N $CaCl_2$. P^H was adjusted finally to the original value with maximum possible accuracy before the last washing. After the final centrifugation, the centrifuge tube containing the washed soil was drained and the occluded solution volume was determined by immediate weighing. The soil samples were then extracted four times with 0.5 N NH_4NO_3. The supernatants were collected and analysed for K,Ca and Chloride. Potassium and calcium was determined by Atomic Absorption and Chloride by titration with $AgNO_3$ in the presence of K_2CrO_4 as indicator. The amounts of cations and anions extracted corrected for the occluded salt solutions were expressed as equivalent amounts of negative and positive charges respectively.

3.2 Statistical analysis

Analysis of variance of the data obtained for the electric charges (CEC and AEC) and inter-relationship of CEC and AEC with varying P^H, and electrolyte concentration for different samples was carried out following the method described by Cochran and Cox (1957).

4. Evaluation of methods of ion exchange measurement

4.1 Samples used.

Fourteen samples representing the A and B horizons of six Ultisols and one Oxisol were used (Table 17).

4.2 Experimental details

Four methods were used for the determination of CEC and AEC at P^H equal to the soil P^H. In addition to this, data on acetate CEC by N NH_4 OAc ($P^H 7$) and ECEC were also taken for comparison. Anion exchange data by phosphate adsorption was also included while making comparison of anion exchange methods.

4.2.1 The compulsive exchange method

This method proposed by Gillman (1979) was later modified by Gillman and Sumpter (1986).

Two grams of soil was placed in a pre-weighed 30 ml centrifuge tube and equilibrated with unbuffered 0.1 M barium chloride solution at an ionic strength approximating that of the soil solution, so that the conditions are made similar to those found in the field. Barium on the exchange complex was then replaced by magnesium when the latter is added as magnesium sulphate without altering the solution ionic strength and P^H. Weighed the tubes to estimate the volume of the entrained solution and after centrifugation, determined magnesium and chloride in the supernatant. CEC and AEC were computed from the volumes of magnesium sulphate used, volume of entrained $BaCl_2$ and the chloride concentration in the final supernatant.

4.2.2 Basic cation exchange capacity (CEC_B) and total cation exchange capacity (CEC_T)

Methods for the measurement of CEC_B (Ca adsorbed), CEC_T (Ca+Al adsorbed) and AEC (Cl^- adsorbed) were introduced by Gillman and Sumpter (1986) and have been described in detail by Gillman and Abel (1987). The same procedure was adopted.

The samples were Ca saturated and brought to equilbrium with 0.002 M $CaCl_2$. The P^H was adjusted to soil P^H (2.5:1; water)and 1 M NH_4NO_3 was then used to extract Al^{3+}, Ca^{2+} and Cl^- from the soil. The amounts adsorbed were calculated after allowing for entrained Al^{3+}, Ca^{2+} and Cl^-.

4.2.3 Electric charges by adsorption of ions from KCl and NaCl

This method proposed by Van Raij and Peech (1972) is a modification of the ion adsorption method suggested by Schofield (1949).

Two grams of oven dry soil was placed in a beaker and 50 ml of 1 N NaCl was added. The P^H was adjusted to the soil P^H by the addition of HCl or NaOH. The next day the P^H was readjusted and the suspension was transferred to a pre- weighed 30ml centrifuge tube. The supernatant was separated by centrifugation. Next the samples were washed three times with 20 ml portions of 0.2 N solution of NaCl or KCl. Readjustments of the P^H, with HCl or NaOH/KOH were made before the last two washings. After the final centrifugation, the tube was drained and immediately weighed. Finally the cations and anions adsorbed were extracted five times with 20 ml of 0.5 N NH_4NO_3. The supernatants were collected in 100 ml volumetric flask and saved for analysis. The amounts sodium/potassium and chloride extracted were expressed as equivalent amounts of negative and positive charges respectively . Thus a total of seven and five methods were tried for the estimation of CEC and AEC respectively. The details of the methods used were as follows:-

CEC	AEC
M1-1N Ammonium acetate (pH7)	M1 - Compulsive exchange
M2-ECEC (sum of cations)	M2 - 0.2 N KCl
M3-Compulsive exchange	M3 - 0.2 N NaCl
M4-0.2 N KCl	M4-"P" adsorption
M5-0.2 N NaCl	M5 - 0.002 M $CaCl_2$
M6-CEC_T	---
M7-CEC_B	---

4.2.4 Statistical analysis.

Analysis of variance was done to compare the effectiveness of different methods for both CEC and AEC determinations.

5. Characterization of permanent and pH dependent charges.

5.1 Details of soils.

Four surface samples representing three Ultisols and one Oxisol were used for this study. The samples used were the Kandiustult-Ap from Pilicode, Plinthustult-Ap from Pilathara, Paleustult-A_1 from Punalur and Haplustox-A_p from Pachalloor.

5.2 Experimental details

Procedure suggested by Uehara and Gillman (1980) was followed. When the solution P^H was adjusted to a value equal to the zpc of the samples, the total net chargeσ_T $\mathcal{T}$ measured was equal to the permanent charge σP. The P^H0 was located from the potentiometric titration curves.

Four grams of oven dry soil in a pre-weighed centrifuge tube with 20 ml of 1 M KCl was shaken for 1 hour. The suspension was centrifuged and supernatant discarded. The residue was washed twice with 20 ml of 0.2 M KCl and then five times with 0.01 M KCl and finally adjusted the P^H to P^H0. When P^H0 and equilibrium was established, removed the supernatant solution and retained for the analysis of K^+ and Cl^-. The tubes were weighed to estimate the entrained KCl solution. The K^+ and Cl^- ions adsorbed were removed with five 20 ml washings of 0.5 M NH_4NO_3 and determined the K^+ and Cl^- in the combined washings. After allowing for the entrained KCl, the $K^+$and Cl^- adsorbed were calculated as cmol (P^+/e^-) Kg^{-1}. Then permanent charge was calculated from the expression $\sigma p = -(K^+ \text{ adsorbed} - Cl^- \text{ adsorbed})$

Permanent charge was also determined by taking the difference between CEC and AEC at P^H0 from the P^H-charge curves of the third experiment. Charge - P^H curves prepared for CEC_T, CEC_B, AEC versus P^H also was used to calculate permanent charge (Gillman and Abel, 1987). A ttempts were also made to calculate σ p by taking the difference between the zero point of titration and zero point of charge from potentiometric titration curves.

Lastly σ p was theoretically calculated from a hybrid model suggested by Uehara and Gillman (1980) for a mixed system consisting of permanent and variable charge components.

6. Contribution of organic matter and sesquioxides to exchange properties of soils.

6.1 Details of samples.

Fourteen samples representing the A and B horizons of six Ultisols and one Oxisol were used for the experiment (Table 20).

6.2 Experimental details.

Four gram samples of soil were transferred to 50 ml beakers and the organic matter was removed by heating over a sand bath with 30 per cent H_2O_2 in 1 M NaOAc buffered at P^H 5 for four hours. The samples were repeatedly washed with distilled water and air dried (Thompson et al.,1989). Another set of samples were repeatedly subjected to Dithionite-citrate-bicarbonate extraction to remove the oxides (Mehra and Jackson,1960). One more set of the samples were subjected to H_2O_2 and dithionite-citrate- bicarbonate treatment to remove organic matter and oxides. All the samples were thoroughly washed with distilled water and air dried. The dried samples in a centrifuge tube were then subjected to CEC and AEC estimation by the compulsive exchange method.

6.3 Statistical analysis.

Simple linear regression and multiple linear regression equations were fitted to relate CEC and AEC to organic carbon and sesquioxides.

7. Mineralogical analysis of clay fraction

7.1 X-ray diffraction analysis (XRDA)

One sample each from all the seven profiles was selected for XRDA. The fine clay for the XRDA was separated as per the procedure outlined by Kunze and Dixon (1986). The clay was suspended in water, washed thoroughly with distilled water and then with 99 per cent ethanol. The suspension was poured on to a slide, air dried andX-rayed using a Philips 1140 X-ray diffractometer using copper Kα radiation. Identificaion of the clay minerals present in the samples was made by calculating the characteristic diagnostic 'd' spacings.

RESULTS

For complete x-ray diffraction analysis of clay two different cation saturations were required, Mg and K, the Mg-clay solvated with glycol in addition. K-saturated samples were further x-rayed after heat treatments.

7.2 Scanning electron microscopic analysis.

The clay samples were dispersed in acetone and this suspension was fixed on brass studs by evaporation with air. These studs were fitted in the circular receptacle of the JFC fine coat iron sputter and gold was coated (Bluish violet flourescence; 8 ma and 8 Kv) for 4 minutes. The studs were then removed, placed in the SEM and scanned for observing the surface features. Observations of the samples were made under different magnifications and SEM pictures were taken in INDU Panchromatic Films (NP 27/120 27 Din 125 ASA).

8. Surface area estimation.

Surface area of 21 samples consisting of one surface sample and two sub-surface samples each from the seven profiles was determined by EGME (Ethylene Glycol Mono- ethyl ether) retention method of Carter et al.(1965). Surface area was also estimated from negative adsorption data solving the quadratic equation.

$$\gamma^- = 6.1 \times 10^{-9} S - \frac{3.774 \times 10^{-17} S^2}{\gamma} \quad \text{where}$$

'S' is the specific surface in $cm^2 100^{-1} g$; 'γ' the total surface charge and γ^- the negative adsorption, both in cmol kg^{-1}. Total surface charge and negative adsorption was determined as per methods detailed by Gillman and Uehara (1980).

RESULTS

1. Charge contributing factors and their inter-relationships

A laboratory study with six selected profiles of Ultisols and one Oxisol representing the important pedological units having wide geographical distribution in the State has been attempted to assess the nature and magnitude of charge, the charge contributing factors and their inter-relationships. The parameters used for the assessment of charge were Cation Exchange Capacity (CEC), Anion Exchange Capacity (AEC), the Effective Cation Exchange Capacity (ECEC), the delta pH and fluoride pH. The charge contributing factors studied were organic matter, clay, Fe_2O_3, Al_2O_3, total R_2O_3, KCl extractable Al and amounts of oxalate and dithionite extractable Fe and Al. These 15 characters of the samples were determined, their inter- correlations worked out and presented in Tables 2 and 3.

1.1 Parameters for the measurement of charge characteristics.

1.1.1 Cation Exchange Capacity (CEC)

The depthwise variation of CEC ranged from 2.1 to 9.6 cmol (P^+) kg^{-1} for the Kandiustult of Pilicode, 2.6 to 6.8 in the Plinthustult of Pilathara, 1.6 to 13.0 for the Paleustult of of Punalur, 1.6 to 5.9 for the Kandiustult of Arackal, 2.3 to 5.9 in the case of the Haplustult of Karakulam, 2.8 to 6.7 for the Kandiustult of Maruthur and 4.1 to 8.7 in the Haplustox of Pachallor. CEC was significantly and positively correlated with ECEC, organic carbon, Fe_o, Al_o, Al_d and fluoride pH. Significant negative correlation was observed between CEC and AEC.

1.1.2. Anion Exchange Capacity (AEC)

The AEC values varied from 0.7 to 2.1 cmol (ē) Kg^{-1} for the Kandiustult of Pilicode, 0.8 to 1.8 for the Plinthustult of Pilathara, 1.2 to 2.4 for the Paleustult of Punalur, 1.0 to 1.8 for the Kandiustult of Arackal, 0.4 to 1.6 for the Haplustult of Karakulam, 0.8 to 2.2 for the Kandiustult of Maruthur and from 1.7 to 2.4 for the Haplustox of Pachalloor. AEC was significantly and positively correlated with Fe_2O_3, Al_2O_3 and R_2O_3. Correlations obtained were significant and negative with ECEC, organic carbon and oxalate and dithionite extractable aluminium.

Table 2. Charge contributing factors and parameters of charge assessment

Soil samples/ Location (1)	Horizon (2)	Δp^H (3)	ECEC cmol (p^+) Kg^{-1} (4)	Exch.Al. cmol(p^+) kg^{-1} (5)	Org. C % (6)	Clay % (7)	Fe_2O_3 % (8)	Al_2O_3 % (9)	R_2O_3 % (10)	Fe_o % (11)	Fe DCB (12)	Al_o (13)	Al DCB (14)	p^H (NaF) (15)	AEC _ cmol(e) kg^{-1} (16)	CEC cmol(P^+) kg^{-1} (17)
Kandiustult (Pilicode)	Ap	-1.6	3.6	0.5	2.0	10.3	13.0	28.0	41.0	0.16	5.4	0.14	1.04	10.8	0.8	9.6
	B_1	-1.6	3.6	1.2	1.6	11.4	9.8	15.1	25.0	0.16	3.8	0.13	0.95	10.4	1.2	7.1
	B_2	-1.9	3.8	1.5	1.0	9.6	13.5	25.3	29.0	0.16	5.8	0.10	0.08	10.6	2.1	4.1
	B_{23}	-1.9	3.8	1.5	0.5	13.4	11.3	21.2	32.5	0.12	3.1	0.10	0.78	9.8	1.6	2.8
	C	-1.8	2.4	0.7	0.2	35.6	6.8	6.8	14.0	0.14	4.1	0.10	0.72	9.6	0.7	2.1
Plinthustult (Pilathara)	Ap	-1.3	4.9	0.9	1.5	13.6	7.0	15.1	22.1	0.16	11.4	0.06	0.80	10.0	0.8	6.8
	B_1	-1.5	2.5	1.2	0.9	14.0	25.3	24.5	49.8	0.14	5.3	0.08	0.05	10.9	1.8	5.3
	B_{21}	-1.8	3.5	1.5	0.7	22.0	16.1	16.4	32.5	0.18	3.4	0.08	0.70	10.2	1.6	5.2
	B_{22}	-1.9	3.4	0.8	0.2	31.6	22.4	23.8	46.0	0.14	3.1	0.08	1.00	9.9	1.7	2.6
Paleustult (Punalur)	A_1	-1.1	6.6	1.5	3.2	11.6	7.0	16.6	24.0	0.22	4.0	0.12	1.12	10.2	1.2	13.0
	A_2	-1.1	4.0	2.0	2.0	17.6	8.5	22.3	30.8	0.12	3.0	0.10	1.02	10.5	1.5	8.9
	Bt_1	-1.2	2.9	1.5	1.0	29.6	9.0	22.7	32.0	0.10	5.5	0.08	0.06	10.6	1.4	5.6
	Bt_2	-1.2	2.4	1.0	0.4	29.0	11.5	28.0	39.5	0.10	4.9	0.04	0.83	9.8	2.4	5.1
	Bt_3	-1.2	2.4	1.3	0.4	31.0	9.3	17.4	26.7	0.10	3.7	0.05	0.84	9.8	1.6	2.4
	Bt_4	-1.2	1.8	1.0	0.2	35.6	8.0	21.4	29.0	0.10	1.8	0.04	0.51	9.7	1.7	1.6

(Contd.)

Table 2. Charge contributing factors and parameters of charge assessment (Contd.)

Soil samples/ Location (1)	Horizon (2)	Δp^H (3)	ECEC cmol (p^+) Kg^{-1} (4)	Exch.Al. cmol(p^+) kg^{-1} (5)	Org. C % (6)	Clay % (7)	Fe_2O_3 % (8)	Al_2O_3 % (9)	R_2O_3 % (10)	Fe_o % (11)	Fe DCB (12)	Al_o (13)	Al DCB (14)	p^H (NaF) (15)	AEC cmol(e⁻) kg^{-1} (16)	CEC cmol(P^+) kg^{-1} (17)
Kandiustult	Ap	-1.2	2.6	0.4	1.1	11.8	6.8	16.8	23.6	0.10	2.3	0.04	0.50	9.8	1.0	5.9
(Arackal)	B_1	-1.3	4.0	0.5	1.1	12.3	8.6	24.6	33.2	0.05	2.9	0.04	0.45	9.6	1.8	4.4
	B_{21}	-1.4	3.6	0.7	0.8	16.4	7.8	26.4	34.2	0.06	4.3	0.03	0.71	8.5	1.8	4.0
	B_{22}	-1.8	4.3	1.3	0.7	17.0	9.0	28.6	37.6	0.08	3.0	0.04	0.45	8.5	1.8	3.1
	B_{23}	-1.4	4.3	0.9	0.3	28.8	8.4	19.8	28.2	0.07	4.0	0.03	0.53	9.9	1.3	2.1
	B_{24}	-1.5	3.6	1.0	0.2	33.0	7.0	23.0	30.0	0.06	2.0	0.04	0.39	9.4	1.5	1.6
	B_{25}	-1.2	3.8	0.7	0.2	34.6	6.4	24.0	30.4	0.06	2.8	0.05	0.31	9.2	1.7	1.6
Haplustult	Ap	-1.9	4.9	0.3	1.3	19.6	5.4	18.3	23.7	0.06	2.6	0.02	0.40	8.8	0.4	5.9
(Karakulam)	B_1	-1.4	6.4	1.5	0.7	39.2	6.2	24.8	31.0	0.06	3.8	0.04	0.42	9.6	1.4	6.1
	B_2	-1.5	6.4	1.8	0.5	38.0	7.3	20.3	27.6	0.06	2.6	0.05	0.39	9.2	1.1	6.6
	B_{23}	-1.5	4.3	1.6	0.3	37.6	6.5	17.8	24.3	0.07	2.8	0.05	0.47	9.3	1.3	4.8
	C	-1.3	5.7	1.6	0.2	31.6	7.1	23.4	30.5	0.08	2.8	0.04	0.38	9.4	1.6	2.3
Kandiustult	Ap	-1.7	4.9	0.9	1.2	29.6	5.8	18.3	24.1	0.08	3.5	0.05	1.13	9.3	0.8	6.7
(Maruthur)	B_1	-1.8	4.7	1.5	0.5	37.6	6.3	23.4	29.7	0.06	4.5	0.04	0.05	9.3	1.5	4.1
	B_2	-1.7	4.1	1.5	0.3	37.0	9.8	21.4	31.2	0.07	5.5	0.05	0.08	9.5	1.6	4.3
	B_{22}	-1.8	3.8	1.4	0.3	27.6	11.3	22.8	34.1	0.08	4.4	0.04	0.50	9.8	2.2	5.9
	C	-1.8	3.0	1.3	0.2	32.0	10.8	17.3	28.1	0.08	7.8	0.04	0.46	9.4	1.4	2.8
Haplustox	Ap	-1.4	2.9	0.3	0.9	23.6	9.8	26.8	36.6	0.10	2.8	0.06	0.55	9.9	2.4	8.7
(Pachalloor)	AB	-1.6	4.8	0.3	0.5	29.6	11.3	22.1	23.4	0.12	3.9	0.06	0.30	9.9	2.0	6.6
	BA	-1.3	3.0	1.3	0.2	21.6	10.6	23.4	34.0	0.10	3.8	0.03	0.27	9.8	2.6	4.6
	B	-1.2	2.0	0.5	0.2	28.0	9.8	23.0	32.8	0.12	5.7	0.04	0.29	9.4	1.7	4.1

Table 3. Correlation coefficient matrix between all pairs of 15 soil characters

	ΔpH	ECEC	KCl-Al	OC %	Clay %	Fe_2O_3 %	Al_2O_3 %	R_2O_3 %	Fe_o%	Fe_d%	Al_o%	Al_d%	pH(NaF)	AEC	CEC
ΔpH		-0.092	-0.026	0.214	-0.017	-0.290	0.100	-0.114	-0013	-0.038	-0.124	0.076	0.147	-0.136	0.202
ECEC			0.320	0.352*	0.061	-0.357*	-0.015	-0.227	-0.094	-0.041	-0.002	0.073	-0.212	-0.315	0.386
KCl-Al				0.021	0.179	0.018	-0.038	-0.011	0.050	0.028	0.168	-0.075	0.156	0.703	0.026
OC %					-0.669**	-0.082	-0.091	-0.102	0.552**	0.144	0.589**	0.487**	0.411*	-0.374*	0.843**
Clay %						-0.243	-0.092	-0.214	-0.525**	-0.180	-0.459**	-0.288	-0.387*	-0.026	-0.440**
Fe_2O_3 %							0.253	0.779**	0.434**	0.141	0.331*	-0.029	0.525**	0.360*	0.034
Al_2O_3 %								0.803**	-0.293	-0.128	-0.191	-0.265	-0.040	0.606**	-0.004
R_2O_3 %									0.083	0.008	0.087	-0.191	0.302	0.615**	-0.017
Fe_o%										0.317	0.790**	0.432**	0.682**	-0.086	0.471**
Fe_d%											0.133	-0.047	0.267	-0.106	0.142
Al_o%												0.442**	0.703**	-0.214	0.473**
Al_d%													0.131	-0.309	0.380*
pH(NaF)														0.074	0.410*
AEC															-0.176
CEC															

** Significant at 1% level
* Significant at 5% level

1.1.3 Effective Cation Exchange Capacity (ECEC)

ECEC values varied from 2.4 to 3.8 cmol (p+) kg-1 in the Kandiustult of Pilicode , 2.5 to 4.9 in the Pilinthustult of Pilathara, 1.8 to 6.6 in the Paleustult of Punalur, 2.6 to 4.3 in the Kandiustult of Arackal, 4.3 to 5.7 in the Haplustult of Karakulam, 3.0 to 4.9 in the Kandiustult of Maruthur and from 2.0 to 4.8 in the Haplustox of Pachalloor. Positively correlated with exchangeable Al, organic carbon and CEC , ECEC showed negative relationship with Fe_2O_3, R_2O_3, AEC and pH (1N NaF).

1.1.4 Delta pH (pH KCl-pH water)

The values varied from -1.6 to -1.9 in the kandiustult of Pilicode, -1.3 to -1.9 in the Plinthustult of Pilathara, -1.1 to -1.2 in the Paleustult of Punalur, -1.3 to -1.8 in the Kandiustult of Arackal, -1.3 to -1.9 in the Haplustult of Karakulam, -1.7 to -1.8 in the Kandiustult of Maruthur and from -1.2 to -1.6 in the Haplustox of Pachalloor. Delta pH was significantly and positively correlated with organic carbon and CEC, but significant negative relationship was observed with Fe_2O_3.

1.1.5 pH 1N NaF

The values ranged from 9.6 to 10.8 in the Kandiustult of Pilicode, 9.9 to 10.9 in the Plinthustult of Pilathara, 9.7 to 10.6 in the Paleustult of Punalur, 8.5 to 9.9 in the Kandiustult of Arackal, 8.8 to 9.6 in the Haplustult of Karakulam, 9.3 to 9.8 in the Kandiustult of Maruthur and from 9.4 to 9.9 in the Haplustox of Pachalloor. Fluoride pH was positively correlated with organic carbon, Fe_2O_3, R_2O_3, Fe_o, Fe_d and Al_o while significant negative correlations were obtained with ECEC and clay percentage.

1.2 Charge contributing factors.

1.2.1 Organic Carbon

A depthwise decrease in organic carbon content was observed in all the profiles studied. The values ranged from 0.2 to 2 per cent in the Kandiustult of Pilicode, 0.2 to 1.5 in the Plinthustult of Pilathara, 0.2 to 3.2 in the Paleustult of Punalur, 0.2 to 1.1 in the Kandiustult of Arackal, 0.2 to 1.3 in the Haplustult of Karakulam, 0.2 to 1.2 in the Kandiustult of Maruthur and 0.2 to 0.9 in the Haplustox of Pachalloor. Organic carbon was found to be significantly and positively correlated with Fe_o, Al_o, Al_d, ECEC and CEC. Significant negative correlations were observed in the case of AEC and clay content.

1.2.2 Clay content.

A depthwise increase in clay content was observed in all the profiles studied. The variation in clay per cent was from 9.6 to 35.6, 13.6 to 31.6, 11.6 to 35.6, 11.8 to 34.6, 19.6 to 39.2, 29.6 to 37.6 and 21.6 to 29.6 for Kandiustult of Pilicode, Plinthustult of Pilathara, Paleustult of Punalur, Kandiustult of Arackal, Haplustult of Karakulam, Kandiustult of Maruthur and Haplustox of Pachalloor respectively. Significant negative correlations were observed with Fe_2o_3, R_2O_3, Fe_o, Al_o, Al_d and fluoride pH in the case of clay content.

1.2.3 Fe_2O_3 content

The values in per cent ranged from 6.8 to 13.5, 7.0 to 25.3, 7.0 to 11.5, 6.8 to 9.0, 5.4 to 7.3, 5.8 to 11.3 and 9.8 to 11.3 for the Kandiustult of Pilicode, Plinthustult of Pilathara, Paleustult of Punalur, Kandiustult of Arackal, Haplustult of Karakulam, Kandiustult of Maruthur and Haplustox of Pachalloor respectively. Fe_2O_3 was significantly and positively corelated with Al_2O_3, R_2O_3, Fe_o, Al_o, fluoride pH and AEC. Significant negative correlations were observed with ECEC and delta pH.

1.2.4 Al_2O_3 per cent.

Values varied from 6.8 to 28.0, 15.1 to 24.5, 16.6 to 28.0, 16.8 to 28.6, 17.8 to 24.8, 17.3 to 23.4 and 22.1 to 26.8 in the Kandiustult of Pilicode, Plinthustult of Pilathara, Paleustult of Punalur, Kandiustult of Arackal, Haplustult of Karakulam, Kandiustult of Maruthur and in the Haplustox of Pachalloor respectively. Al_2O_3 showed significant positive correlations with R_2O_3 and AEC while negative correlations were observed with Fe_o and Al_d.

1.2.5. Total sesquioxide (R_2O_3) per cent.

Values varied from 14.0 to 41.0, 22.1 to 49.8, 24.0 to 39.5, 23.6 to 37.6, 23.7 to 30.5, 24.1 to 34.1 and 32.8 to 36.6 for the Kandiustult of Pilicode, Plinthustult of Pilathara, Paleustult of Punalur, Kandiustult of Arackal, Haplustult of Karakulam, Kandiustult of Maruthur and for the Haplustox of Pachalloor respectively.

R_2O_3 per cent was found to give significant positive correlation with Fe_2O_3, Al_2O_3, fluoride pH and AEC. It was negatively correlated with CEC, ECEC, clay content and organic carbon.

1.2.6. KCl Extractable Al

Values ranged from 0.5 to 1.5 cmol (P^+) kg^{-1} for the Kandiustult of Pilicode, 0.8 to 1.5 for the Plinthustult of Pilathara, 1.0 to 2.0 for the Paleustult of punalur, 0.4 to 1.3 for the Kandiustult of Arackal, 0.3 to 1.8 for the Haplustult of Karakulam, 0.9 to 1.5 for the Kandiustult of Maruthur and from 0.3 to 1.3 for the Haplustox of Pachalloor. Significant positive correlation was observed between KCl-Al and ECEC. Though not significant, positive correlations were also observed with Al_o, clay content and fluoride pH.

1.2.7. Oxalate Extractable Fe (Fe_o) per cent.

Values varied from 0.12 to 0.16, 0.14 to 0.18, 0.10 to 0.22, 0.05 to 0.10. 0.06 to 0.08, 0.06 to 0.08 and from 0.10 to 0.12 in the Kandiustult of Pilicode, Plinthustult of Pilathara, Paleüstult of Punalur, Kandiustult of Arackal, Haplustult of Karakulam, Kandiustult of Maruthur and Haplustox of Pachalloor respectively. Significant positive correlations were observed with CEC, Fe_2O_3, organic carbon, Al_o, Al_d and Fe_d. Correlations obtained were significant and negative with Al_2O_3 and clay content.

1.2.8 Dithionite Extractable Fe(Fe_d) per cent.

Content ranged from 3.10 to 5.80 in the Kandiustult of Pilicode, 3.05 to 11.35 in the Plinthustult of Pilathara, 1.80 to 5.50 in the Paleustult of Punalur, 2.00 to 4.29 in the Kandiustult of Arackal, 2.60 to 3.82 in the Haplustult of Karakulam, 3.50 to 7.80 in the Kandiustult of Maruthur and from 2.80 to 5.67 in the Haplustox of Pachalloor. Fe_d was positively correlated with Fe_o, fluoride pH and organic carbon whereas negatively with AEC, clay content and Al_2O_3 percentage.

1.2.9 Oxalate Extractable Al (Al_o) per cent.

Values ranged from 0.1 to 0.14 in the Kandiustult of Pilicode, 0.06 to 0.08 in the Plinthustult of Pilathara, 0.04 to 0.12 in the Paleustult of Punalur, 0.03 to 0.05 in the Kandiustult of Arackal, 0.02 to 0.05 in the Haplustult of karakulam, 0.04 to 0.05 in the Kandiustult of Maruthur and from 0.03 to0.06 in the Haplustox of Pachalloor. Significant positive correlations were observed with Al_d, fluoride pH, CEC, Fe_o, Fe_2O_3 and organic carbon. It was negatively correlated with AEC and Al_2O_3 though the correlations were not significant.

Table 4. Some physical and chemical characteristics of the samples(For other characteristics refer to table 2)

Samples/ Location	Horizon	pH					E.C	Sand	Silt	Clay	Exch. cations cmol (P⁺) Kg⁻¹			
		Water		1M KCl	0.01M $CaCl_2$	1M NaF	dsm⁻¹	%	%	%	Ca	Mg	K	Na
		1:1	1:2.5	1:2.5	1:2.5	1:50								
Kandiustult (Pilicode)	Ap	5.0	5.8	4.2	4.2	10.2	0.06	81.4	4.8	10.3	2.08	0.82	0.08	0.11
	B_1	5.2	5.8	4.2	4.1	10.4	0.04	80.6	8.0	11.4	1.66	0.64	0.04	0.10
	B_2	5.6	5.8	3.9	4.0	10.6	0.08	81.4	9.0	9.6	1.43	0.77	0.04	0.13
	B_{23}	5.2	5.9	4.0	4.0	9.8	0.08	78.6	8.0	13.4	1.60	0.61	0.03	0.10
	C	5.4	5.8	4.0	4.2	9.6	0.06	56.4	8.0	35.6	1.05	0.52	0.03	0.11
Plinthustult (Pilathara)	Ap	4.6	5.1	3.8	4.0	10.0	0.05	72.4	14.0	13.6	3.20	0.64	0.06	0.12
	B_1	4.6	5.1	3.6	3.8	10.9	0.06	74.0	12.0	14.0	0.98	0.24	0.04	0.09
	B_{21}	4.8	5.3	3.5	3.7	10.2	0.08	64.0	14.0	22.0	1.50	0.33	0.05	0.14
	B_{22}	5.5	5.6	3.7	3.9	9.9	0.08	54.4	14.0	31.6	2.00	0.49	0.04	0.10
Paleustult (Punalur)	A_1	4.8	5.2	4.1	4.0	10.2	0.20	80.4	6.0	11.6	3.35	1.56	0.09	0.09
	A_2	4.9	5.2	4.1	3.9	10.5	0.14	74.4	8.0	17.6	1.28	0.58	0.05	0.09
	Bt_1	5.1	5.3	4.1	3.9	10.0	0.14	64.4	6.0	29.6	0.53	0.77	0.03	0.10
	Bt_2	5.3	5.5	4.3	4.0	9.8	0.18	63.0	8.0	29.0	0.28	0.39	0.03	0.08
	Bt_3	5.2	5.4	4.2	3.9	9.8	0.05	58.0	11.0	31.0	0.46	0.62	0.03	0.08
	Bt_4	5.1	5.4	4.2	3.9	9.7	0.09	49.0	15.0	35.6	0.35	0.34	0.03	0.08

(Contd.)

Table 4. Some physical and chemical characteristics of the samples(For other characteristics refer to table 2) (Contd.)

Samples/ Location	Horizon	pH					E.C	Sand	Silt	Clay	Exch. cations cmol (P⁺) Kg⁻¹			
		Water		1M KCl	0.01M CaCl₂	1M NaF	dsm⁻¹	%	%	%	Ca	Mg	K	Na
		1:1	1:2.5	1:2.5	1:2.5	1:50								
Kandiustult (Pilicode)	Ap	4.8	5.6	4.4	4.4	9.8	0.14	79.2	9.0	11.8	1.32	0.75	0.05	0.12
	B_1	4.9	5.7	4.4	4.5	9.6	0.12	76.7	11.0	12.3	1.52	1.66	0.23	0.16
	B_{21}	4.6	5.4	4.0	4.0	8.5	0.08	73.6	10.0	16.4	1.60	1.08	0.10	0.14
	B_{22}	4.7	5.6	3.8	3.9	8.5	0.08	74.0	9.0	17.0	1.57	1.27	0.07	0.13
	B_{23}	4.6	5.4	4.0	4.1	9.9	0.08	58.2	13.0	28.8	2.23	1.03	0.04	0.11
	B_{24}	4.7	5.4	3.9	4.1	9.4	0.08	53.0	14.0	33.0	1.63	0.86	0.04	0.10
	B_{25}	4.6	5.3	4.1	4.2	9.2	0.08	50.4	15.0	34.6	0.96	0.40	0.05	0.18
Haplustult (Karakulam)	Ap	5.3	5.6	3.7	3.4	8.8	0.14	68.4	12.0	19.6	2.36	1.39	0.70	0.12
	B_1	4.9	5.3	3.9	3.5	9.0	0.16	49.4	10.0	39.2	1.87	1.64	0.29	0.10
	B_2	4.7	5.4	3.9	3.5	9.2	0.05	51.0	11.0	38.0	0.81	0.63	0.08	0.11
	B_{23}	4.4	5.3	3.8	3.5	9.3	0.21	52.0	10.0	37.6	1.0	0.50	0.04	0.11
	C	4.3	5.3	4.0	3.6	9.4	0.19	58.4	9.6	31.6	1.05	1.62	0.34	0.12
Kandiustult (Maruthur)	Ap	4.4	5.3	3.6	3.7	9.3	0.03	62.4	8.0	29.6	2.90	0.90	0.11	0.10
	B_1	4.5	5.4	3.6	3.7	9.3	0.06	53.4	9.0	37.6	1.15	0.93	0.05	0.12
	B_2	4.4	5.3	3.6	3.7	9.3	0.08	54.0	9.0	37.0	1.26	1.24	0.03	0.12
	B_{22}	4.5	5.4	3.6	3.7	9.4	0.06	64.4	8.0	27.6	0.49	0.83	0.03	0.13
	C	4.9	5.4	3.6	3.6	9.4	0.08	60.0	8.0	32.0	0.92	0.58	0.05	0.19
Haplustox (Pachalloor)	Ap	4.1	4.8	3.4	3.8	9.1	0.08	68.4	8.0	23.6	1.38	0.61	0.53	0.16
	AB	4.3	5.1	3.5	3.9	9.1	0.14	62.4	8.0	29.6	0.96	0.45	0.24	0.17
	BA	4.1	4.8	3.5	3.9	9.4	0.16	66.4	12.0	21.6	1.01	0.47	0.07	0.16
	B	3.9	4.6	3.4	3.8	9.4	0.18	64.0	8.0	28.0	0.95	0.41	0.03	0.12

1.2.10 Dithionite Extractable Al (Al_d) per cent.

Values varied from 0.08 to 1.04, 0.05 to 1.0, 0.06 to 1.12, 0.31 to 0.71, 0.38 to 0.47, 0.05 to 1.13 and from 0.27 to 0.55 in the Kandiustult of Pilicode, Plinthustult of Pilathara, Paleustult of Punalur, Kandiustult of Arackal, Haplustult of Karakulam, Kandiustult of Maruthur and Haplustox of Pachalloor respectively.

Correlations obtained with CEC, Al_o, Fe_o and organic carbon were significant and positive while negative correlations were observed with AEC, Al_2O_3, R_2O_3 and clay content.

1.2.11. Other physico-chemical characteristics.

Data on pH, EC, granulometric composition and the exchangeable cations suite of the profiles is given in Table 4. An increase in clay content with depth was observed in all the seven profiles. The sand fraction showed a decrease in content with depth and the surface horizons of all the profiles registered the highest value. Silt percentage also increased with depth though the increase was only marginal.

The pH value of all the samples were in the acidic range, pH water was greater than pH KCl and pH $CaCl_2$. pH water was higher with a soil : water ratio of 1:2.5 than with 1:1, while pH KCl and pH $CaCl_2$ recorded more or less the same values. A slight increase in pH was noticed in the sub-surface horizons of all profiles.

Delta pH (pH KCl - pH water) showed negative values for all the samples. Though much variations were not oberved, delta pH values were in general higher for the surface horizons than the sub-surface samples.

Electrical conductivity was very low and not much variation was observed with depth, though a slight increase was noticed for sub-surface horizons.

Exchangeable cations were higher in the surface horizons than the sub-surface horizons.The relative abundance of the cations was in the decreasing order of Ca>Mg> Na>K. An unusual observation that was found in the study was the increase in the percentage base saturation with depth in all the profiles. Values of ECEC has exceeded the CEC in all the samples for the lowest depth.

1.3 Charge contributing factors in relation tothe major parameters of charge measurements

The direct and indirect effects of the various charge contributing factors to the major parameters of charge measurement namely CEC and AEC were brought out by path coefficient analysis.

1.3.1. The direct and indirect effects of charge contributing factors on cation exchange capacity

The correlation matrix between different charge contributing factors is presented in Table 3 and the path coefficient analysis showing the direct and indirect effects of charge contributing factors on CEC is given in Table 5.

From the path coefficient analysis given in Table 5 it was observed that the maximum positive direct effect on CEC (0.973) with a significant positive correlation (0.843) was recorded in the case of organic carbon. The indirect negative effects of R_2O_3 (0.109) was not sufficient to cause a substantial reduction in the correlation coefficient. Al_2O_3 through its positive indirect effect has further influenced the CEC.

Clay content clearly indicated a positive direct effect (0.317) though its effect was nullified and made negative by the indirect negative effects especially of R_2O_3 followed by organic carbon.

Fe_2O_3 and Al_2O_3 of the soils had contributed negative direct effects (-2.270 and -2.236 respectively) on the CEC. The direct effect of KCl extractable Al was also negative (-0.083) though not significant. Both oxalate extractable Fe and Al registered positive correlations (0.471 and 0.473 respectively) with a direct positive effect (0.171) in the former case and a direct negative effect (- 0.280) in the latter. It also influenced the CEC by its indirect positive effects through Al_2O_3, organic carbon and R_2O_3 (0.654, 0.537 and 0.306 respectively) in the case of the oxalate extractable iron, while Al_2O_3 and R_2O_3 (0.428 and 0.321 respectively) contributed the indirect positive effects for the oxalate extractable Al.

Delta pH influenced CEC positively through direct and indirect effects. The correlation was positive though not significant. Maximum negative indirect effect was contributed by R_2O_3 (-0.417) and positive indirect effect was chiefly through Fe_2O_3 (0.659). Fluoride pH indicated a direct positive effect (0.248) on CEC. Positive indirect effects were contributed from R_2O_3 (1.109) and organic carbon (0.400). Table 6 represents the abstract of the path coefficient analysis showing the direct and indirect effects of charge contributing factors on CEC. The residual effect was 45.9 per cent.

Table.5. Path Coefficient analysis showing the direct and indirect effects of charge contributing factors on CEC

	ΔpH	ECEC	KCl-Al	OC%	clay%	Fe_2O_3%	Al_2O_3%	R_2O_3%	Fe_o%	Fe_d%	Al_o%	Al_d%	pH (NaF)	r	Residual effect
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ΔpH	0.086	-0.008	0.002	0.208	-0.005	0.659	-0.223	-0.417	-0.002	0.000	0.035	0.003	0.037	0.202	
ECEC	0.008	0.093	-0.026	0.342	0.019	0.811	0.034	-0.832	-0.016	0.000	0.000	0.003	-0.053	0.386*	
KCl-Al	0.002	0.030	-0.082	0.020	0.057	-0.040	0.085	-0.040	0.008	0.000	-0.047	-0.003	-0.053	0.026	
OC%	-0.018	0.033	-0.002	0.973	-0.212	0.185	0.204	-0.374	0.014	-0.002	-0.165	0.024	0.102	0.843**	
Clay%	0.001	0.006	-0.015	-0.651	0.317	0.551	0.206	-0.786	-0.089	0.002	0.128	-0.014	-0.096	-0.440**	0.459
Fe_2O_3%	0.025	0.033	-0.001	-0.079	-0.076	-2.270	-0.565	2.858	0.074	-0.002	-0.092	-0.001	0.103	-0.034	
Al_2O_3%	-0.009	-0.001	0.003	-0.009	-0.029	-0.573	-2.235	2.948	-0.050	0.002	0.054	-0.013	-0.010	-0.004	
R_2O_3%	0.010.	-0.021	0.000	-0.099	-0.068	-1.768	-1.796	3.669	0.014	0.000	-0.024	-0.009	0.075	-0.017	
Fe_o%	0.001	-0.009	-0.004	0.537	-0.166	-0.985	0.654	0.306	0.171	-0.004	-0.221	0.021	0.169	0.471**	
Fe_d%	0.003	-0.004	-0.002	0.140	-0.057	-0.321	0.285	0.029	0.054	-0.012	-0.037	-0.002	0.066	0.142	
Al_o%	0.011	0.000	-0.014	0.573	-0.145	-0.750	0.428	0.321	0.135	-0.002	-0.279	0.022	0.175	0.473**	
Al_d%	-0.007	0.007	0.006	0.474	-0.091	0.067	0.592	-0.702	0.074	0.001	-0.124	0.050	0.033	0.380*	
pH (NaF)	-0.013	-0.020	-0.013	0.400	-0.123	-1.192	0.090	1.109	0.117	-0.003.	-0.197	0.006	0.248	0.410*	

** significant at 1% level
significant at 5% levle

Table 6. Path coefficient analysis (abstract) showing the direct and indirect effects on cation exchange capacity.

Factors	Direct effect	Total indirect effect	Maximum indirect effect		Correlation coefficient	Remarks
			Positive	Negative		
Δ pH	0.086	0.116	Fe_2O_3	R_2O_3	0.202	—
ECEC	0.093	0.293	Fe_2O_3 followed by organic carbon	R_2O_3	0.386	—
KCl-Al	-0.083	0.109	Al_2O_3	Al_o	0.026	'r' positive direct effect negative.
Organic Carbon	0.973	-0.130	Al_2O_3	R_2O_3	0.843	—
Clay%	0.317	-0.757	Fe_2O_3 followed by Al_2O_3	R_2O_3 followed by organic carbon	-0.440	'r' negative, direct efffect positive.
Fe_2O_3%	-2.270	2.236	R_2O_3	Al_2O_3	-0.034	Indirect effect reduces the 'r'.
Al_2O_3%	-2.236	2.232	R_2O_3	Fe_2O_3	-0.004	Indirect effect reduces the 'r'
R_2O_3%	3.669	-3.686	—	Al_2O_3 and Fe_2O_3	-0.017	Indirect effect reduces the 'r'
Fe_o%	0.171	0.300	Al_2O_3 followed by organic carbon and R_2O_3	Fe_2O_3	0.471	—
Fe_d%	-0.122	0.264	Al_2O_3	Fe_2O_3	0.142	Direct effect negative 'r' is positive
Al_d%	0.050	0.330	Al_2O_3 followed by organic carbon	R_2O_3	0.380	Indirect effect is responsible for the high 'r'
Al_o%	-0.280	0.753	Al_2O_3 followed by R_2O_3	Fe_2O_3	0.473	Direct effect negative and 'r' is positive
pH (NaF)	0.248	0.162	R_2O_3 followed by organic carbon	Fe_2O_3	0.410	—

1.3.2 The direct and indirect effects of charge contributing factors on anion exchange capacity.

The path coefficient analysis given in Table 7 revealed that the R_2O_3% had the maximum positive direct effect (13.095) on the AEC of soils studied. Significant positive correlation was observed with R_2O_3 (0.615) and AEC. However the expression of the direct positive effect of R_2O_3 was considerably influenced through the negative indirect effects of Fe_2O_3 followed by Al_2O_3 (-6.328 and -6.314 respectively). As the direct effect of R_2O_3 was so pronounced, the total net effect and correlation was made positive. Al_2O_3 contributed a negative direct effect (- 7.859) on AEC. However the total indirect effect was positive (8.466). Maximum positive indirect effect was through R_2O_3 (10.520) while maximum negative indirect effect was contributed by Fe_2O_3, the effects of other factors being less pronounced. Extremely high and positive indirect effect had resulted in a net positive and significant correlation in spite of an equally negative direct effect.

The contribution of Fe_2O_3 was also in a similar manner as that of Al_2O_3 with a negative direct effect (- 8.125). The correlation was made significant and positive (0.360) by the highly positive indirect effect (8.485) chiefly contributed by the R_2O_3%.

Organic carbon contributed a negative direct effect (-0.621) to AEC apart from its indirect positive influence through Fe_2O_3 (0.663) and Al_2O_3 (0.717). Organic carbon was significantly and negatively correlated with AEC. Direct negative effect of organic carbon was more than the correlation coefficient.

The direct effect of KCl-Al (0.224) though not significant was also positive. It influenced AEC through its indirect negative effect contributed by R_2O_3 followed by Fe_2O_3. However the direct effect was more pronounced and greater than the correlation coefficient (0.103). Fluoride pH contributed positive direct effect on AEC (0.203). The total indirect effect was negative (-0.129) and influenced through Fe_2O_3 followed by organic carbon and delta pH. The direct effect was greater than the correlation coefficient. The residual effect was 52.18 per cent. Table 8 represents the abstract of the path coefficient analysis showing the direct and indirect effects of charge conrtibuting factors on AEC.

2. Potentiometric titrations.

The data on net electric charge and zpc of the samples, as determined by the potentiometric titrations are shown in Figures 4 to 17 and Appendix 1 to 14. It is evident from the data given in the appendix that the zero point of titration did not coincide with zpc. In all the cases the zpc was displaced towards the acid side of the curve, from the

Table 7. Path Coefficient analysis showing the direct and indirect effects of charge contributing factors on AEC

	Δ pH	ECEC	KCl-Al	OC%	clay%	Fe_2O_3%	Al_2O_3%	R_2O_3%	Fe_o%	Fe_d%	Al_o%	Al_d%	pH (NaF)	r	Residual effect
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Δ pH	0.072	0.011	−0.006	−0.133	0.003	2.360	−0.784	−1.488	−0.008	0.007	0.068	0.007	0.030	0.136	
ECEC	−0.007	−0.124	0.071	−0.218	−0.011	2.903	0.120	−2.967	−0.054	0.007	0.001	0.007	−0.042	−0.315	
KCl-Al	−0.002	−0.039	0.224	−0.013	−0.033	−0.144	0.297	−0.144	0.029	−0.005	−0.091	−0.007	0.032	0.103	
OC%	0.015	−0.044	0.005	−0.621	0.121	0.622	0.717	−1.336	0.320	−0.026	−0.321	0.048	0.083	−0.374*	
Clay%	0.001	−0.008	0.040	0.415	−0.182	1.971	0.725	−2.806	−0.304	0.032	0.250	−0.028	−0.078	0.026	
Fe_2O_3%	−0.020	0.044	0.004	0.050	0.044	−8.125	−1.985	10.198	0.251	−0.025	−0.080	−0.002	0.106	0.360*	0.522
Al_2O_3%	0.007	0.001	−0.008	0.066	0.014	−2.052	−7.859	10.520	−0.169	0.023	0.104	−0.026	−0.080	0.606**	
R_2O_3%	−0.008	0.028	−0.002	0.063	0.039	−6.328	−6.314	13.095	0.048	−0.001	−0.048	−0.019	0.061	0.615**	
Fe_o%	−0.001	0.012	0.001	−0.343	0.096	−3.524	2.299	1.091	0.579	−0.057	−0.431	0.043	0.138	−0.086	
Fe_d%	−0.003	0.005	0.006	−0.089	0.033	−1.147	1.004	0.103	0.184	−0.179	−0.072	−0.004	0.054	−0.106	
Al_o%	−0.008	0.000	0.038	−0.366	0.084	−2.685	1.504	1.144	0.458	−0.024	−0.545	0.043	0.143	−0.214	
Al_d%	0.005	−0.009	−0.017	−0.302	0.052	0.238	2.083	−2.504	0.250	0.008	−0.241	0.099	0.027	−0.309	
NaF)	0.010	0.026	0.035	−0.255	0.071	−4.268	0.316	3.958	0.395	−0.048	−0.383	0.013	0.203	0.074	

** Significant at 1% level

* Significant at 5 % level

Table 8. Path coefficient analysis showing the direct and indirect effects of charge contributing factors on anion exchange capacity (abstract)

Factors	Direct effect	Total indirect effect	Maximum indirect effect		correlation coefficient 'r'	Remarks
			Positive	Negative		
ΔpH	0.072	0.064	Fe_2O_3	Al_2O_3	0.136	——
ECEC	-0.124	-0.190	Fe_2O_3	R_2O_3	-0.315	——
Kcl-Al	0.224	-0.121	Al_2O_3	R_2O_3 followed by Fe_2O_3	0.103	Direct effect more than 'r'
Organic carbon%	-0.621	0.247	Al_2O_3 followed by Fe_2O_3	R_2O_3	-0.374	Direct effect more than 'r'
Clay %	-0.182	0.155	Fe_2O_3 followed by Al_2O_3 and organic carbon.	R_2O_3	0.026	Direct effect negative 'r' is positive
Fe_2O_3 %	-8.125	8.485	R_2O_3	Al_2O_3	0.360	Direct effect negative 'r' is positive
Al_2O_3 %	-7.859	8.466	R_2O_3	Fe_2O_3	0.606	Direct effect negative 'r' is positive
R_2O_3 %	13.095	-12.480	—	Fe_2O_3 followed by Al_2O_3	0.615	Direct effect nullified by the negative indirect effects of Fe_2O_3 and Al_2O_3

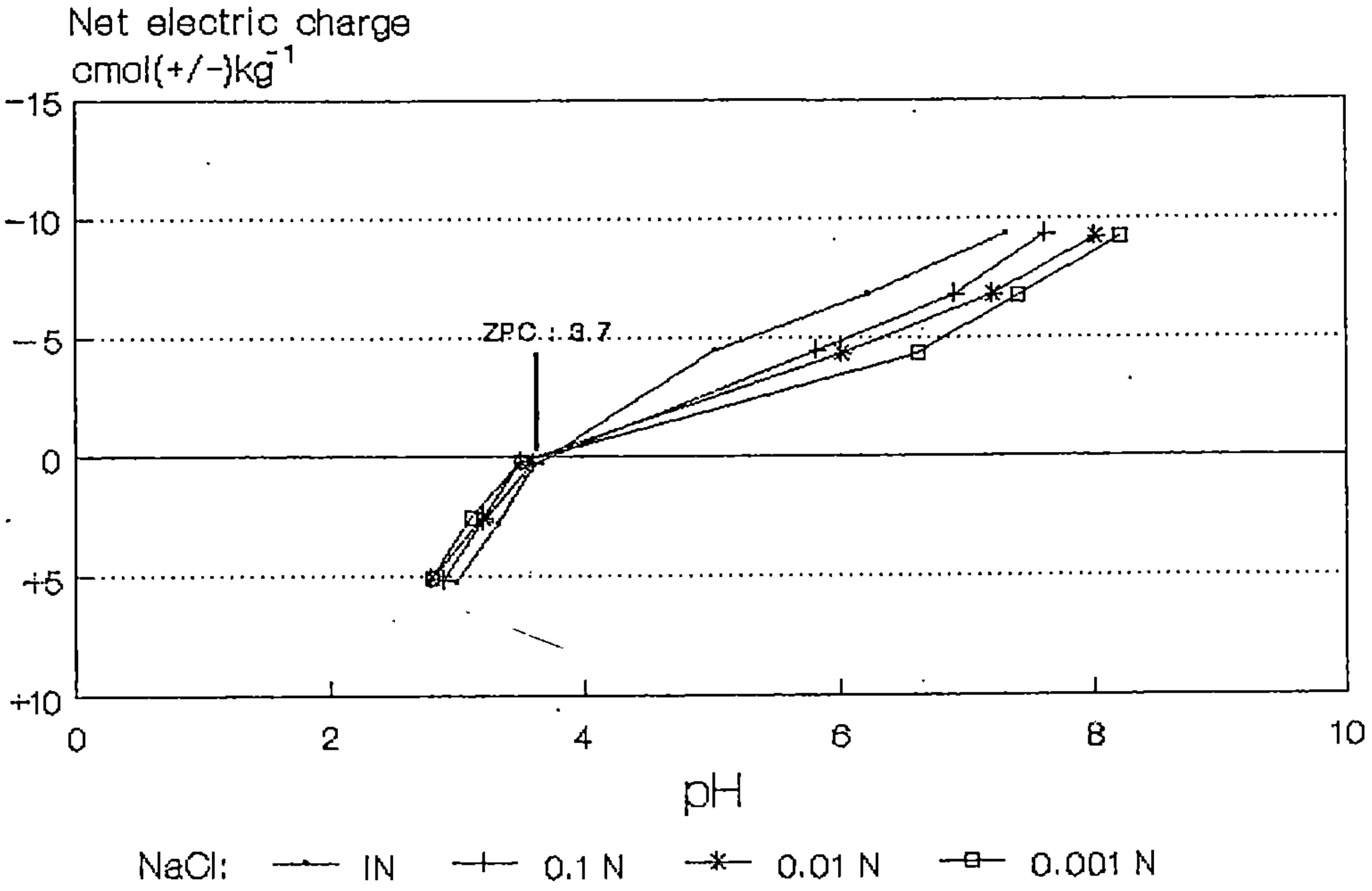
(Contd.)

Table 8. Path coefficient analysis showing the direct and indirect effects of charge contributing factors on anion exchange capacity (abstract)

(Contd.)

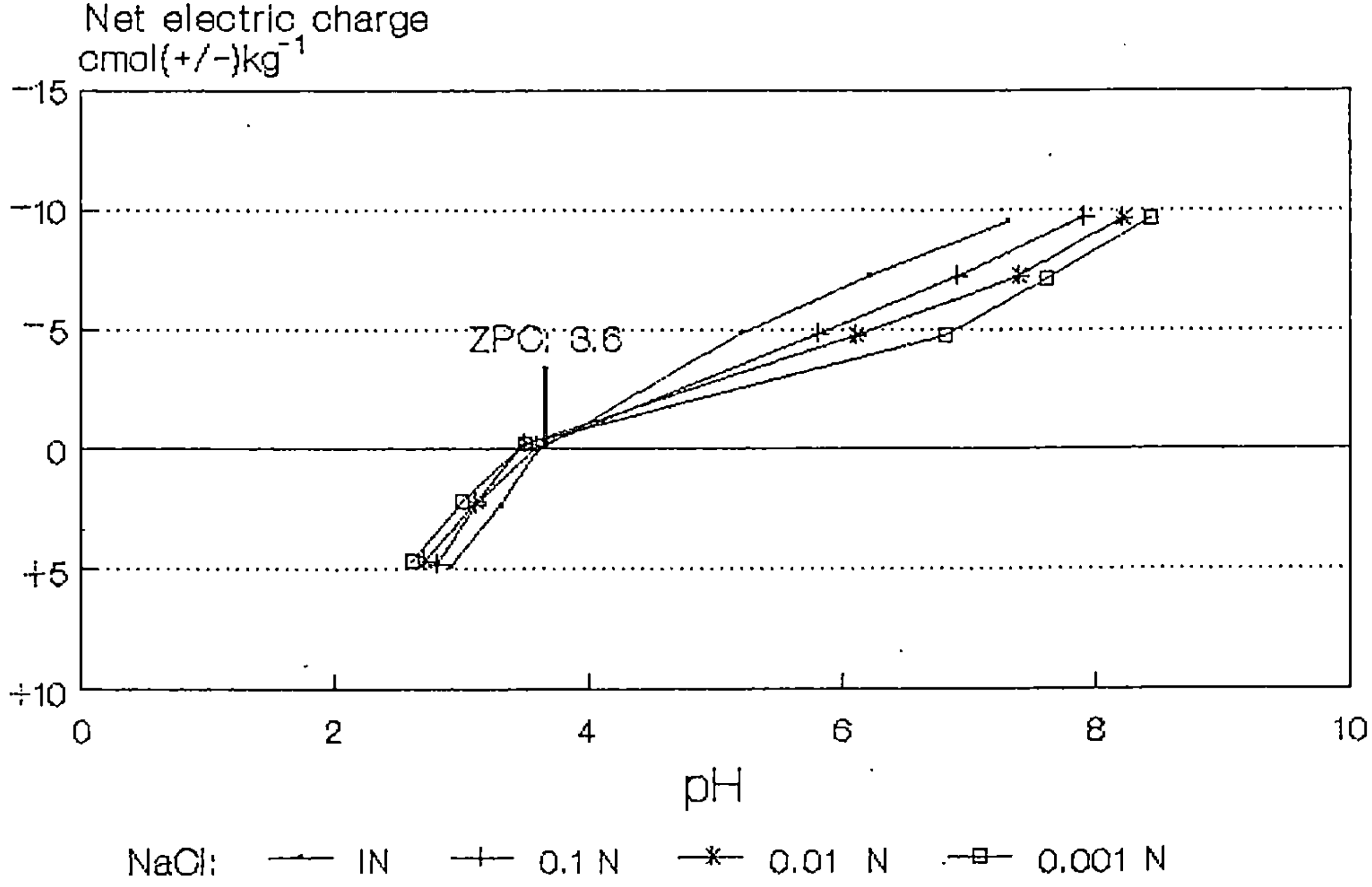
Factors	Direct effect	Total indirect effect	Maximum indirect effect		correlation coefficient 'r'	Remarks
			Positive	Negative		
Fe_o %	0.379	−0.665	Al_2O_3 followed by R_2O_3	Fe_2O_3	−0.086	Direct effect positive, 'r' is less and negative
Fe_d %	−0.179	0.073	Al_2O_3	Fe_2O_3	−0.106	Direct effect and 'r' both negative
Al_o %	−0.545	0.331	Al_2O_3 followed by R_2O_3	Fe_2O_3	−0.214	Direct effect and 'r' negative. Direct effect greater than 'r'
Al_d %	0.099	−0.409	Al_2O_3	R_2O_3	−0.309	Direct effect positive 'r' is negative, 'r' greater than direct effect
p^H (NaF)	0.203	−0.129	Al_2O_3 followed by R_2O_3 and Fe_o	Fe_2O_3 followed by Organic carbon and p^H	0.074	Direct effect greater than 'r' and positive

Fig. 4 : Net electric charge as a function of pH and concentration of Sodium Chloride



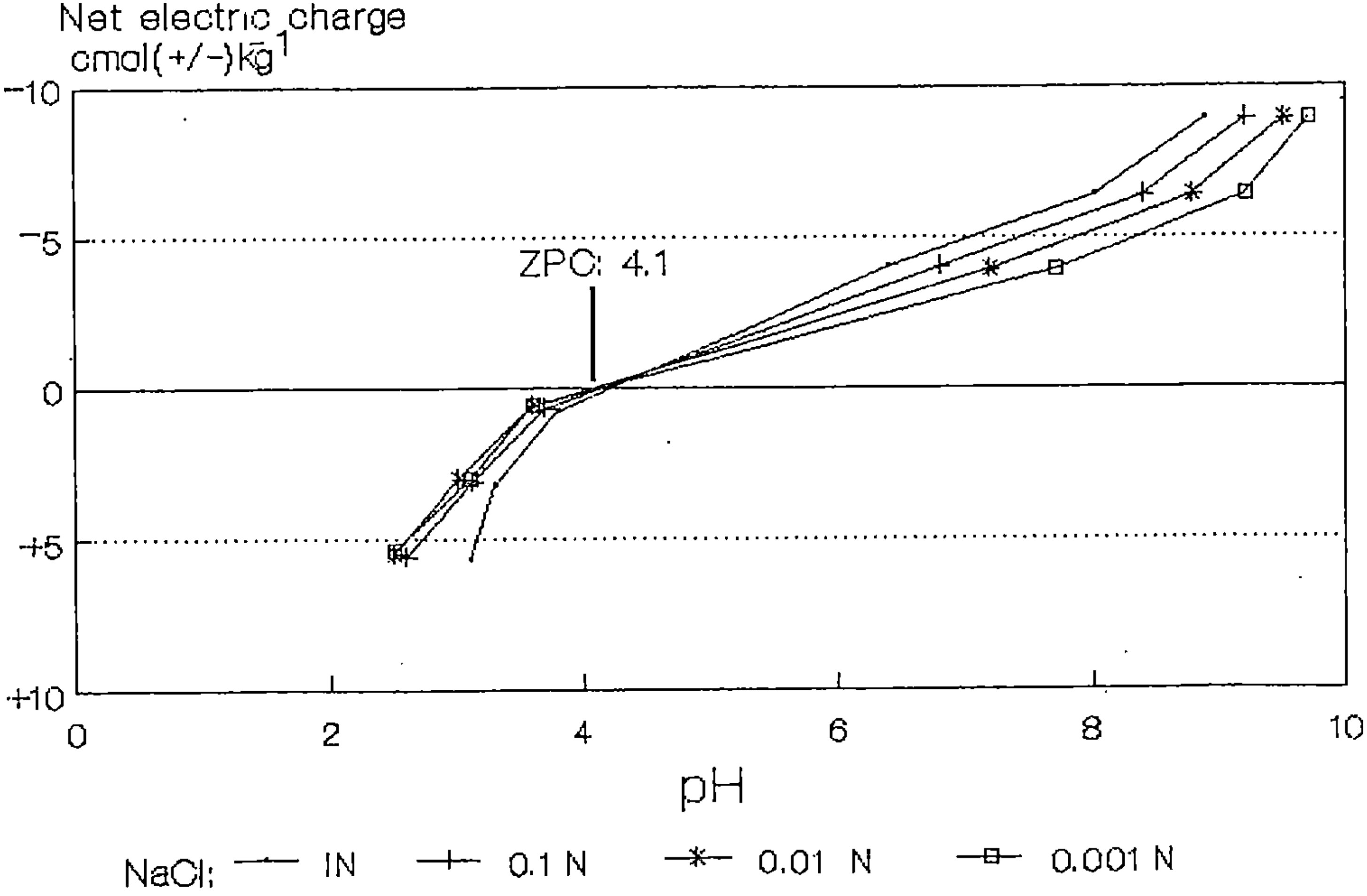
KANDIUSTULT - Ap (Pilicode)

Fig. 6 : Net electric charge as a function of pH and concentration of Sodium Chloride



PLINTHUSTULT - Ap (Pilathara)

Fig. 5 : Net electric charge as a function of pH and concentration of Sodium Chloride



KANDIUSTULT - B_2 (Pilicode)

Fig. 7 : Net electric charge as a function of pH and concentration of Sodium Chloride

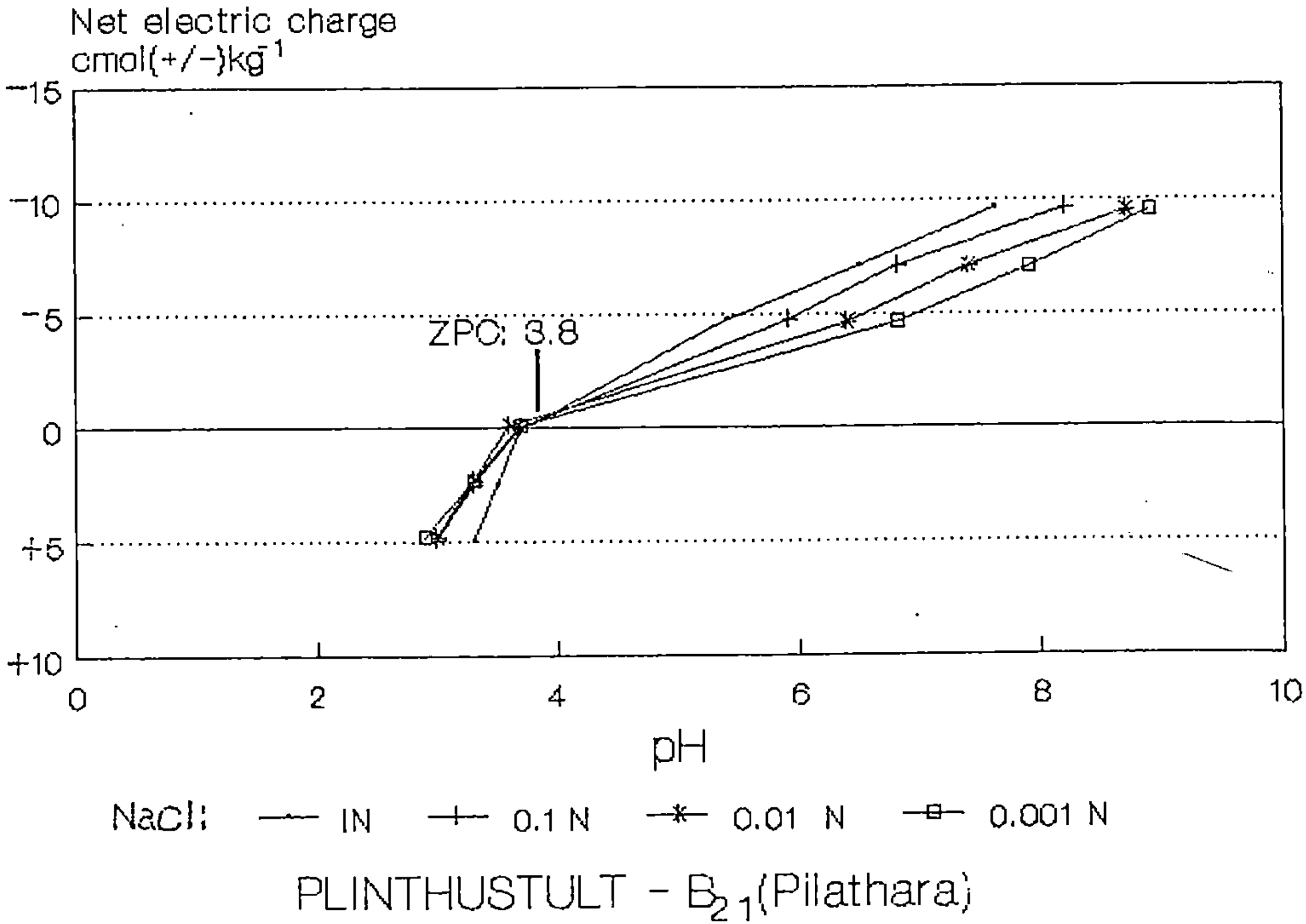
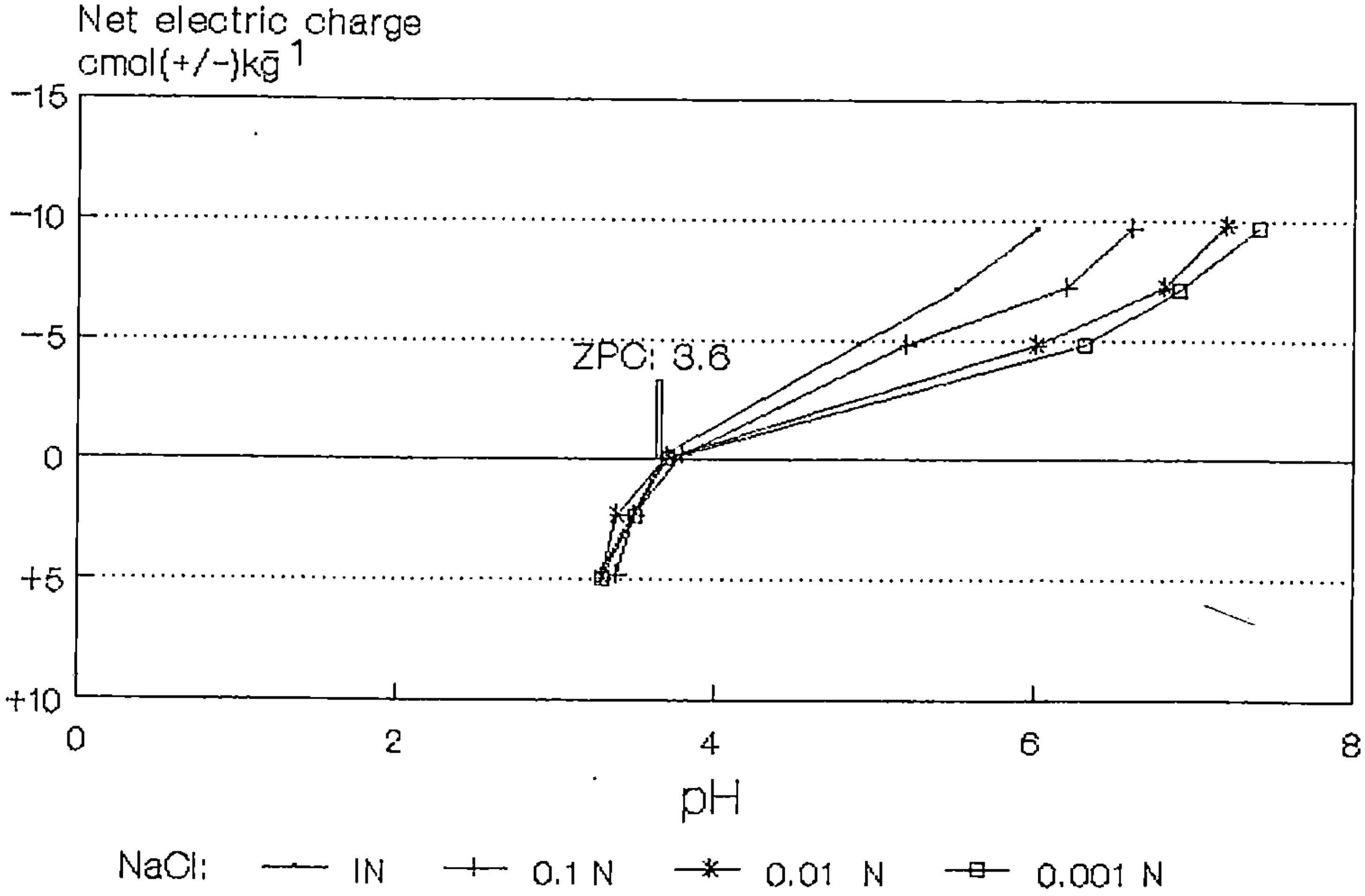
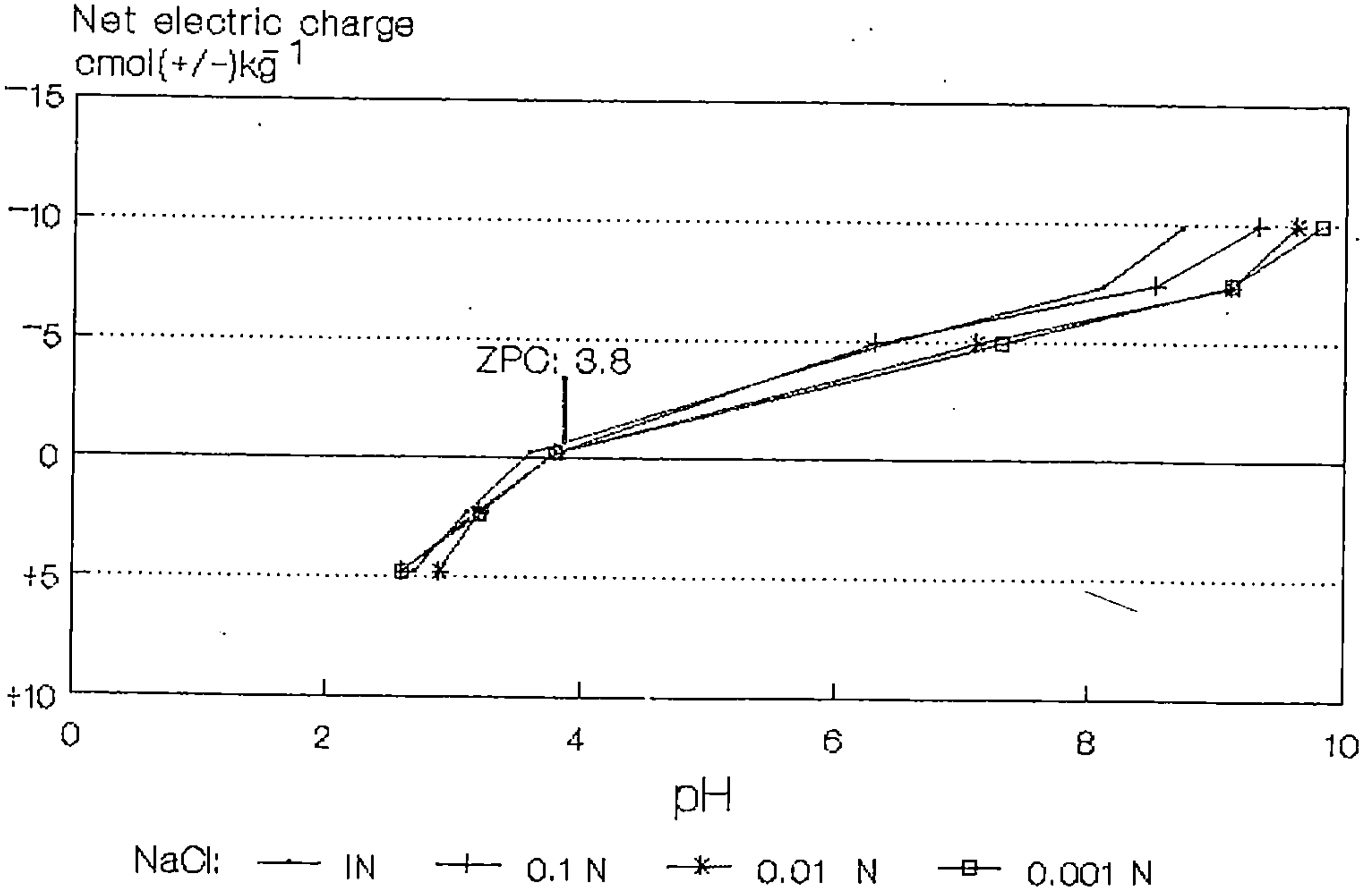


Fig. 8 : Net electric charge as a function of pH and concentration of Sodium Chloride



PALEUSTULT - A1 (Punalur)

Fig. 9 : Net electric charge as a function of pH and concentration of Sodium Chloride



PALEUSTULT - B_{t2} (Punalur)

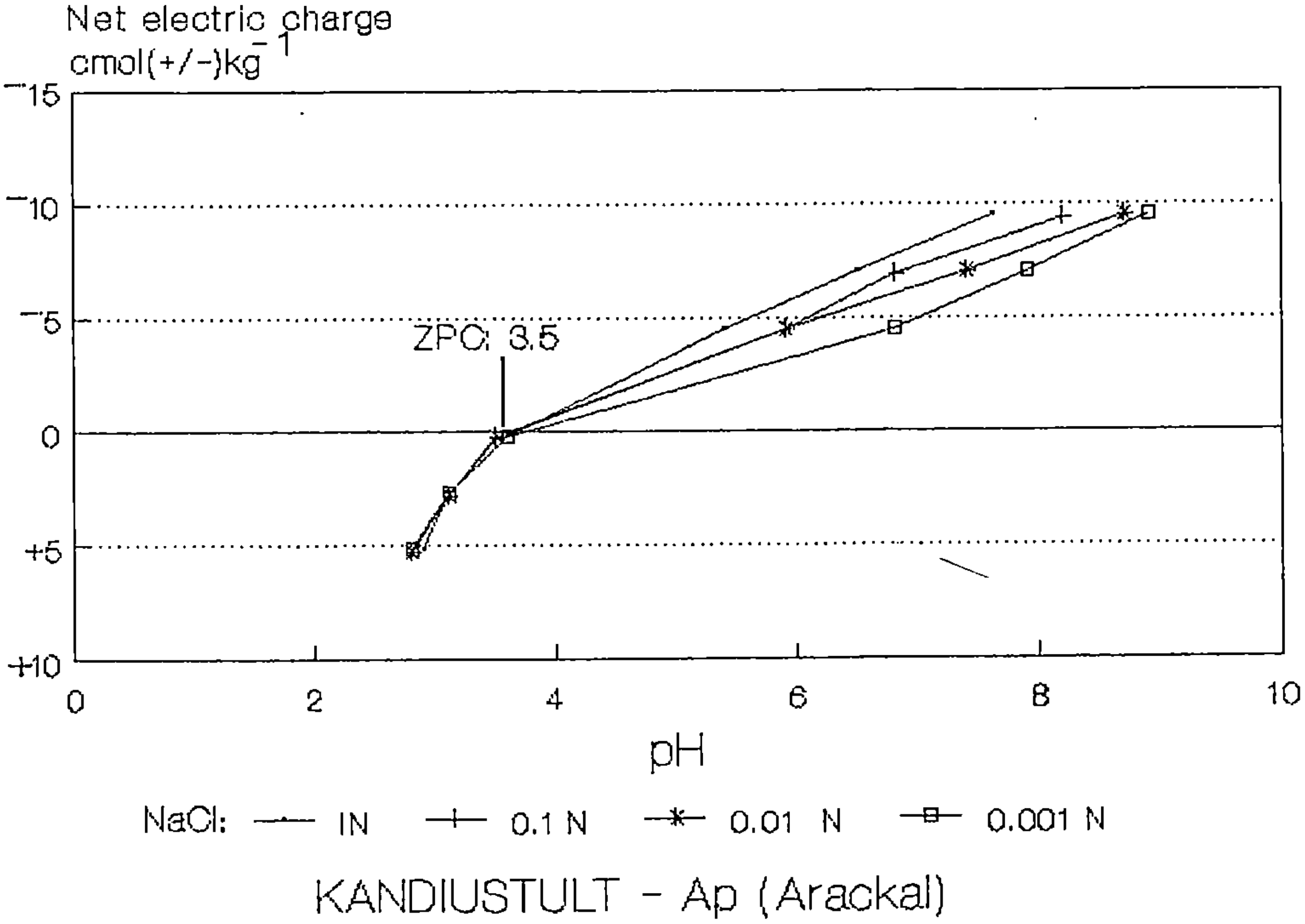
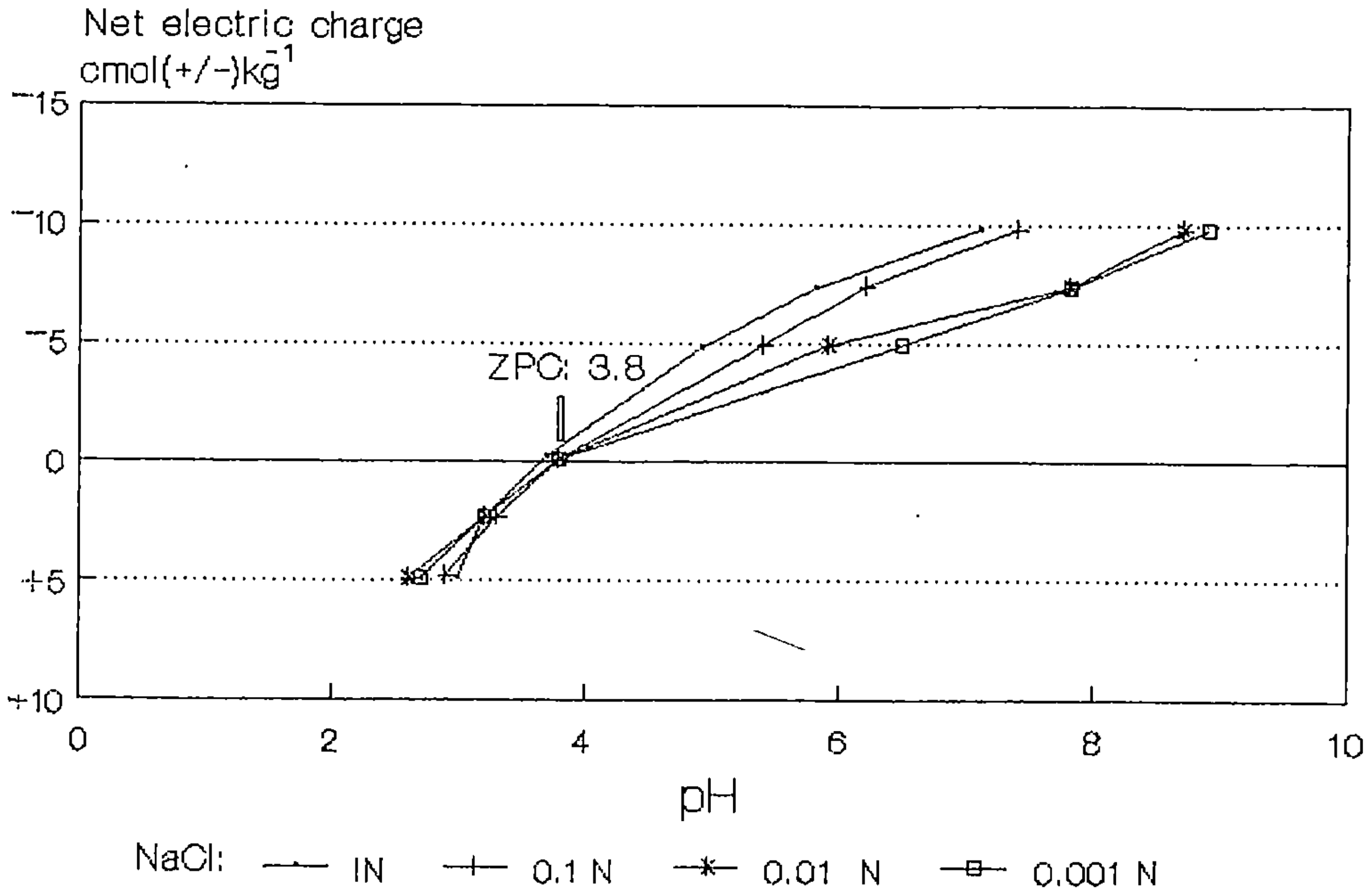


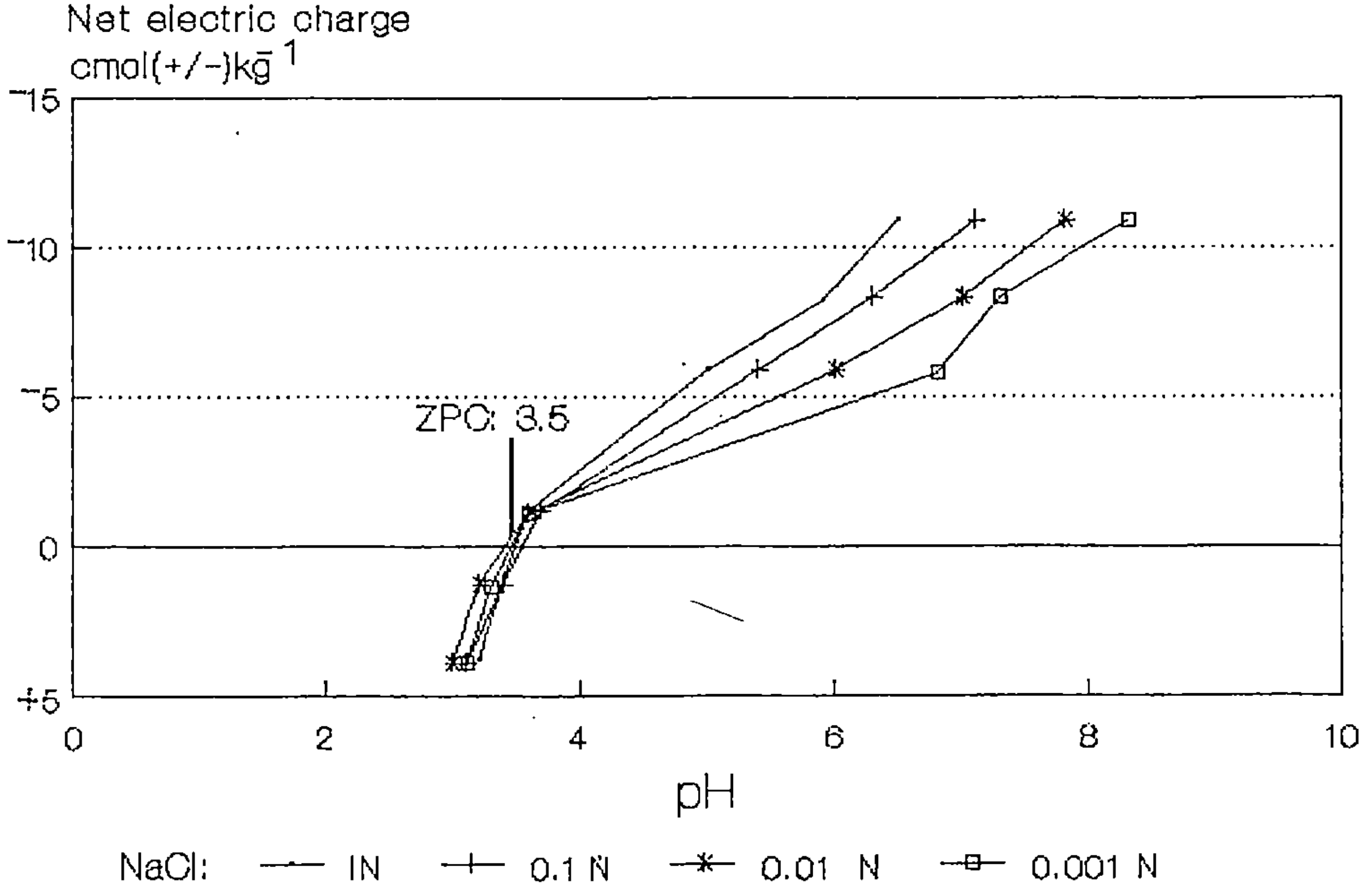
Fig. 10 : Net electric charge as a function of pH and concentration of Sodium Chloride

Fig. 11 : Net electric charge as a function of pH and concentration of Sodium Chloride



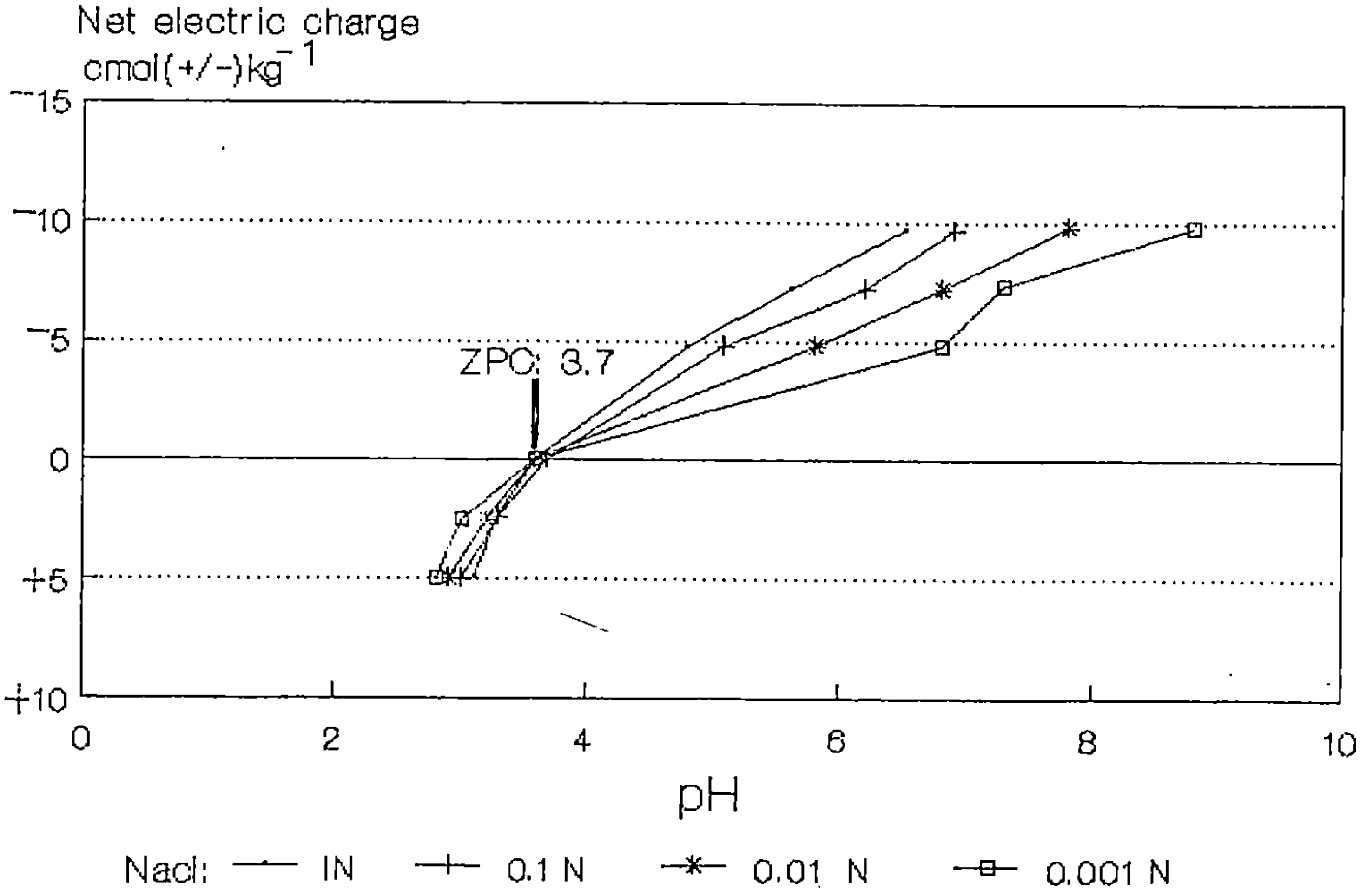
KANDIUSTULT - B_{22} (Arackal)

Fig. 12 : Net electric charge as a function of pH and concentration of Sodium Chloride



HAPLUSTULT - Ap (Karakulam)

Fig. 13 : Net electric charge as a function of pH and concentration of Sodium Chloride



HAPLUSTULT - B_2 (Karakulam)

Fig. 14 : Net electric charge as a function of pH and concentration of Sodium Chloride

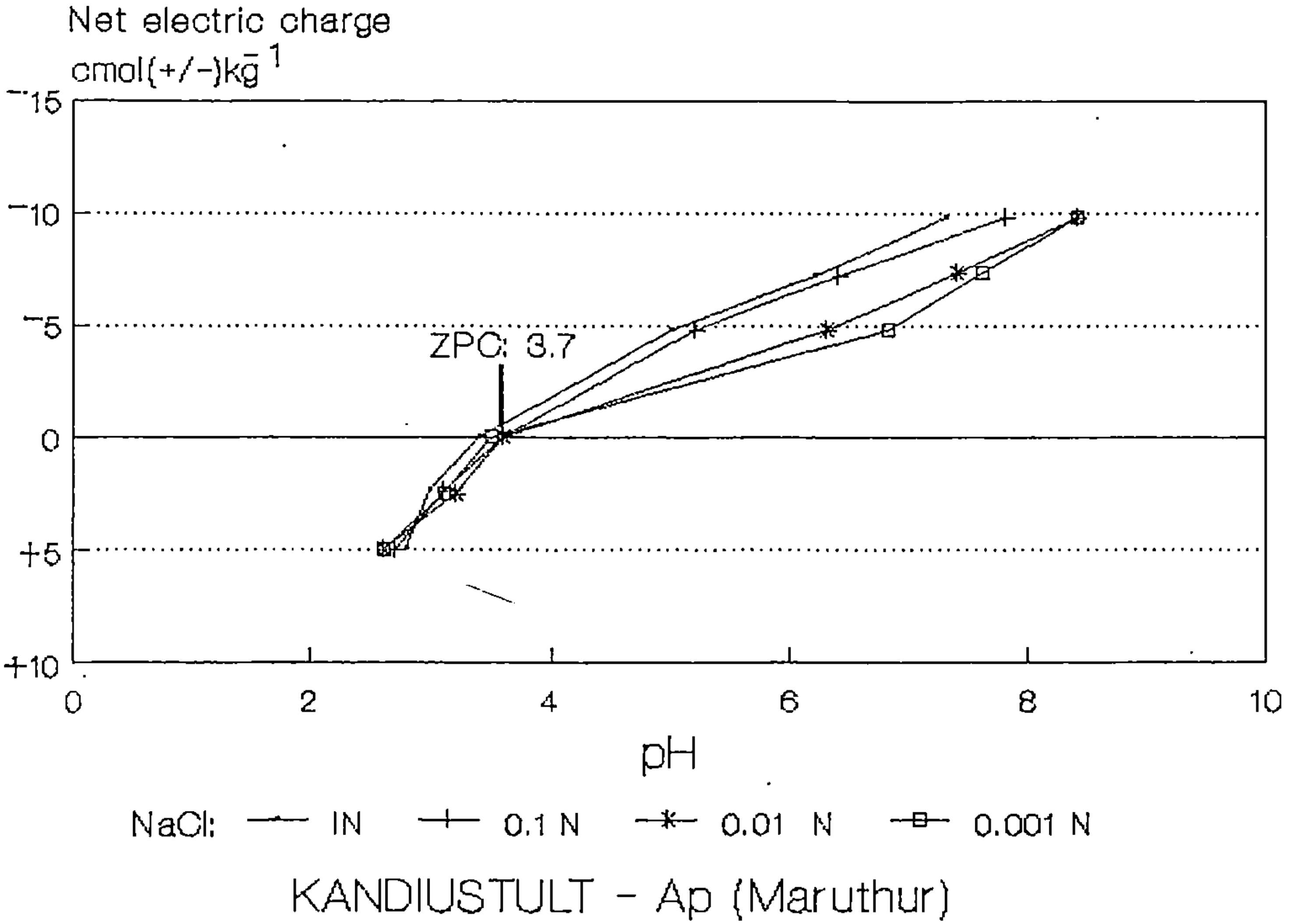
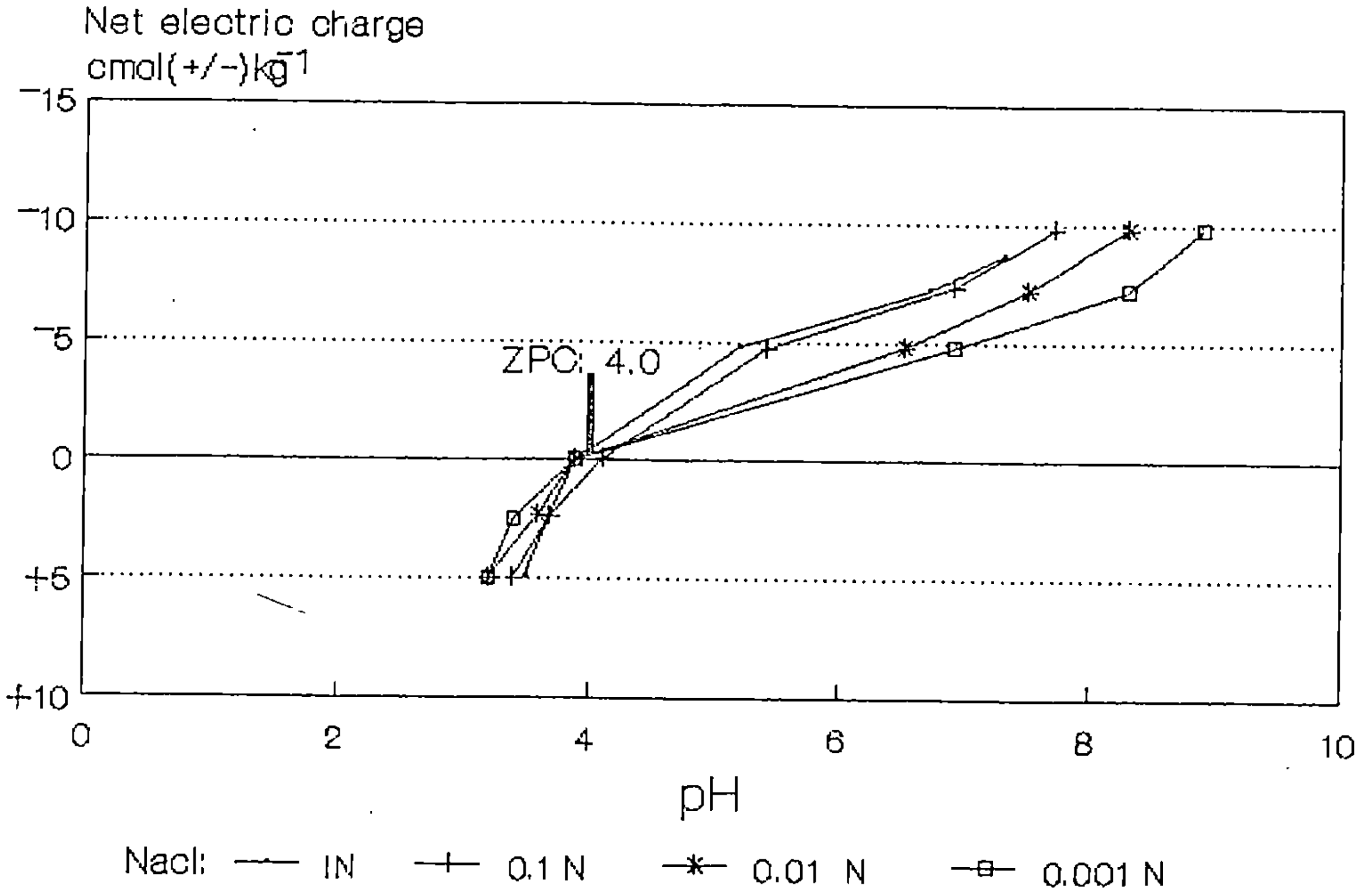


Fig. 15 : Net electric charge as a function of pH and concentration of Sodium Chloride



KANDIUSTULT - B_2 (Maruthur)

Fig. 16 : Net electric charge as a function of pH and concentration of Sodium Chloride

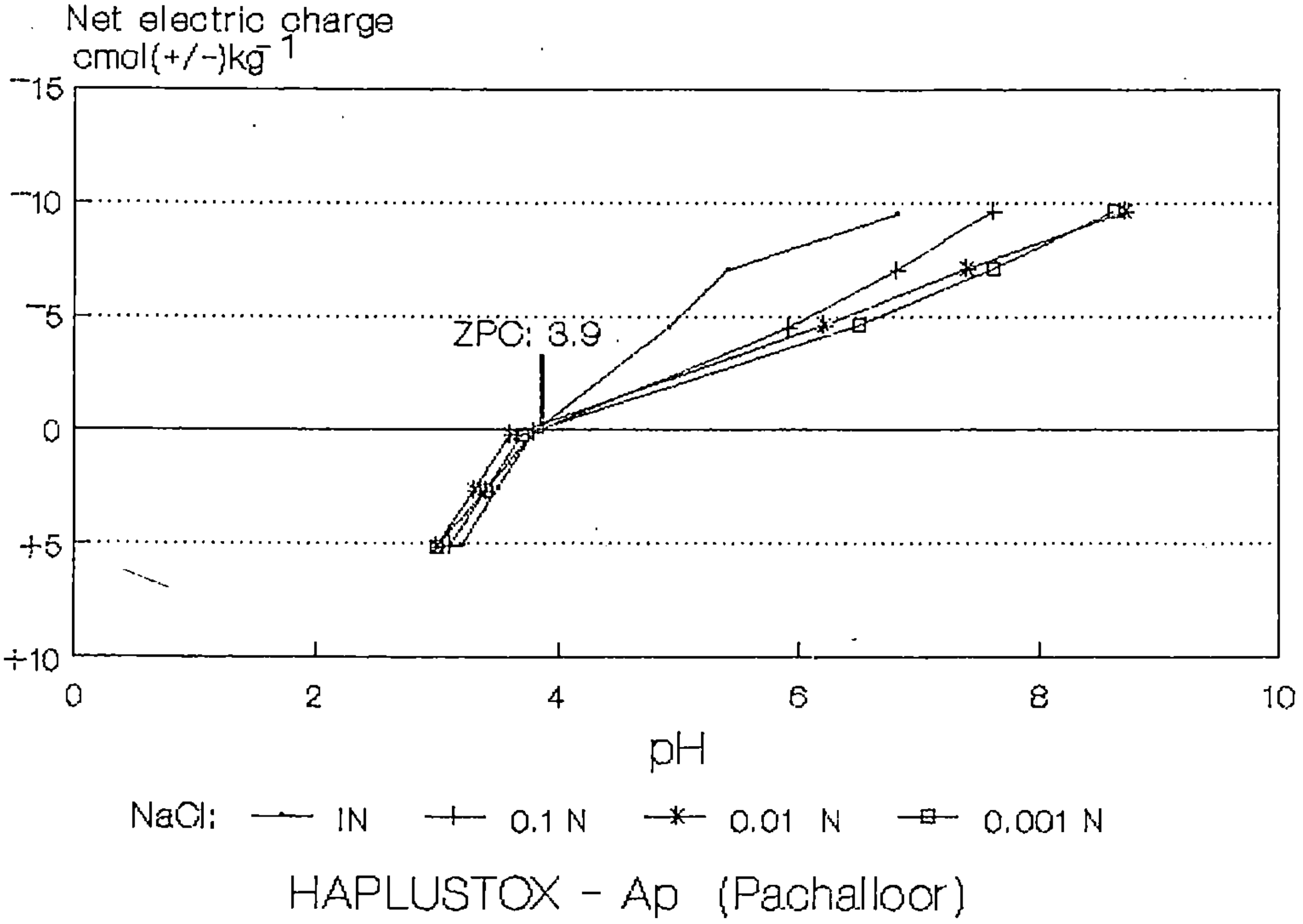
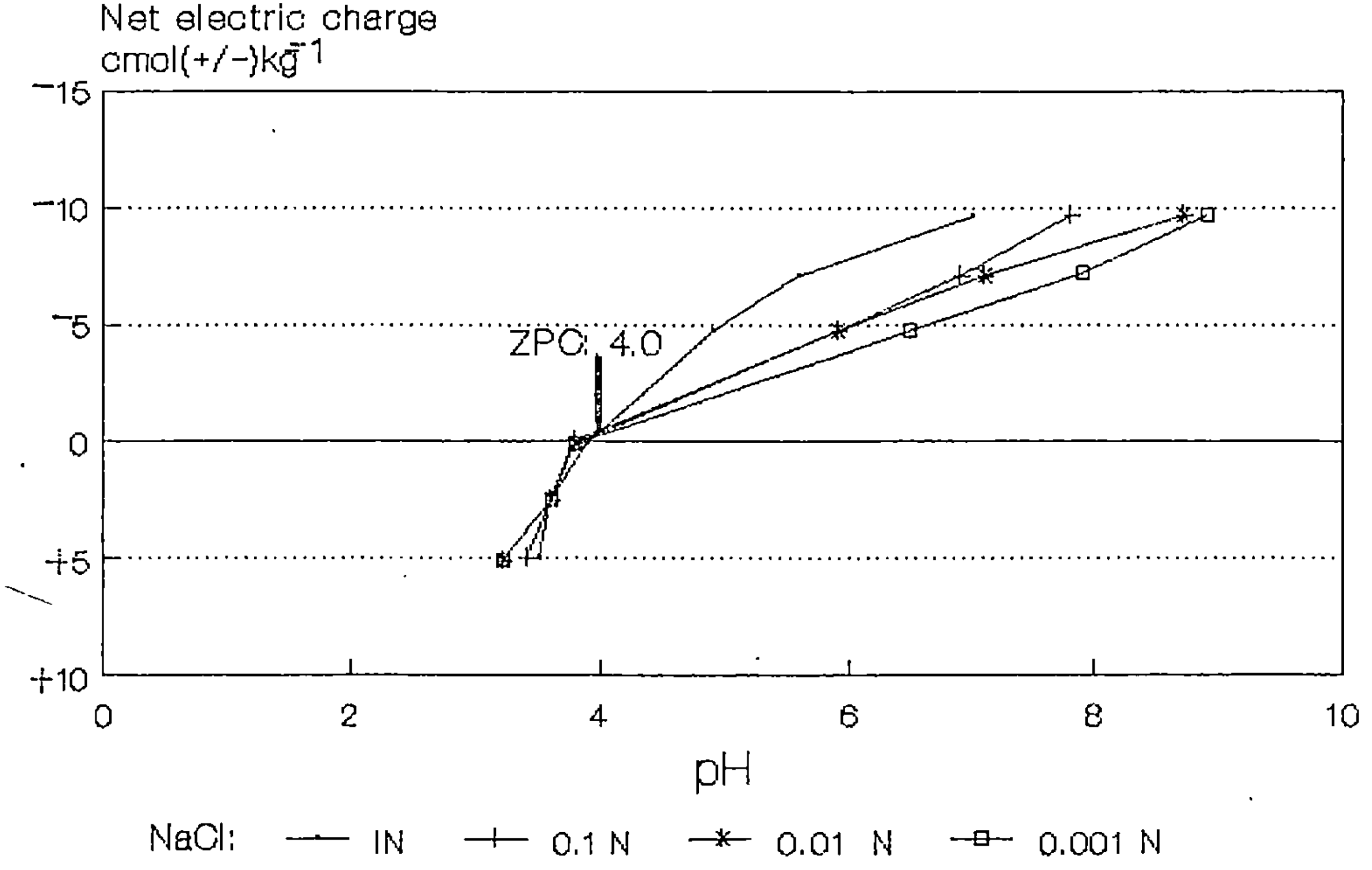


Fig. 17 : Net electric charge as a function of pH and concentration of Sodium Chloride



HAPLUSTOX - BA (Pachalloor)

Fig. 18 (a) Experimental and theoretical net negative charge against double layer potential (1 N NaCl)

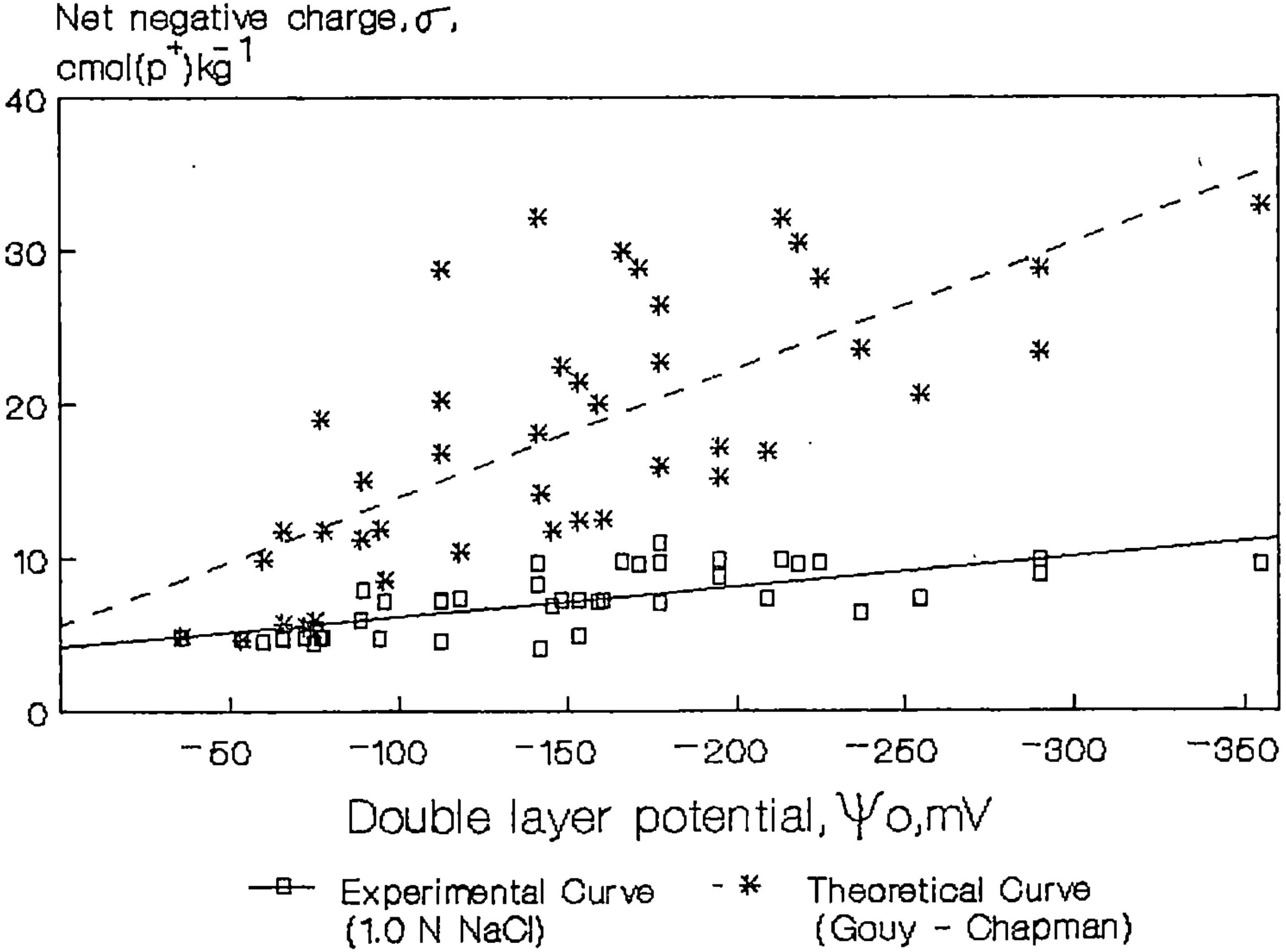


Fig. 18 (b) Experimental and theoretical net negative charge against double layer potential (0.1 N NaCl)

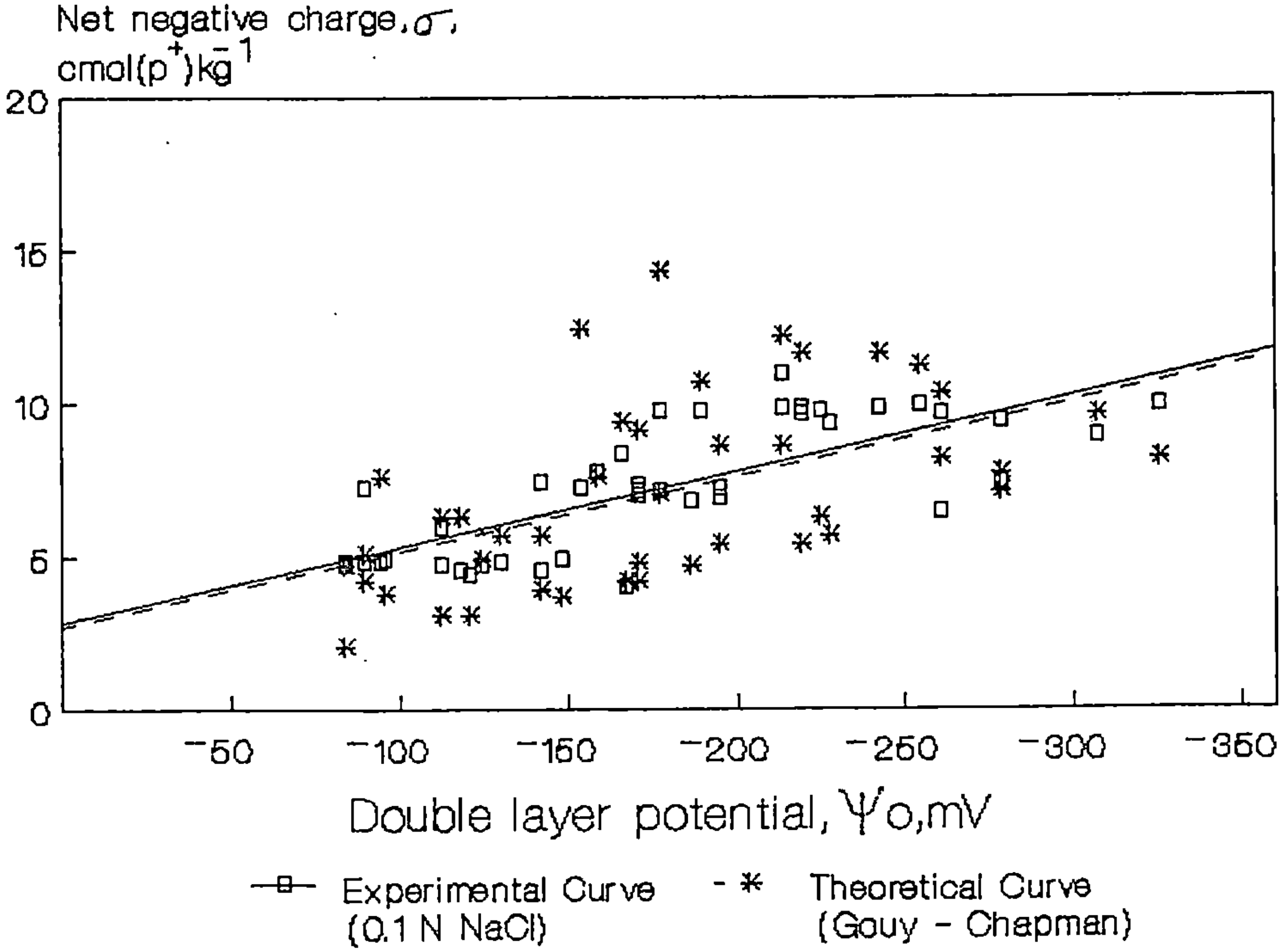


Fig. 19 (a) Experimental and theoretical net negative charge against double layer potential (0.01 N NaCl)

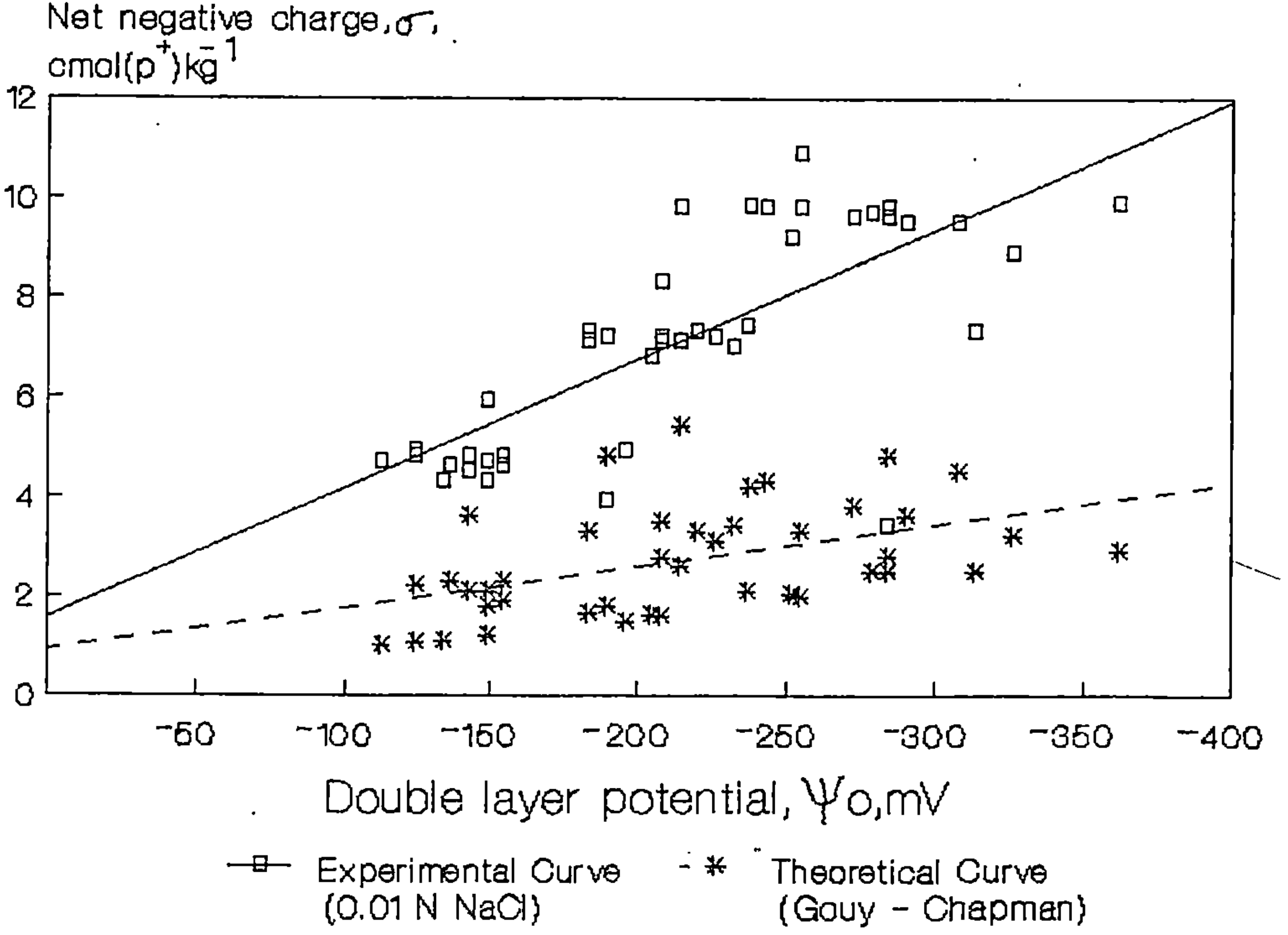
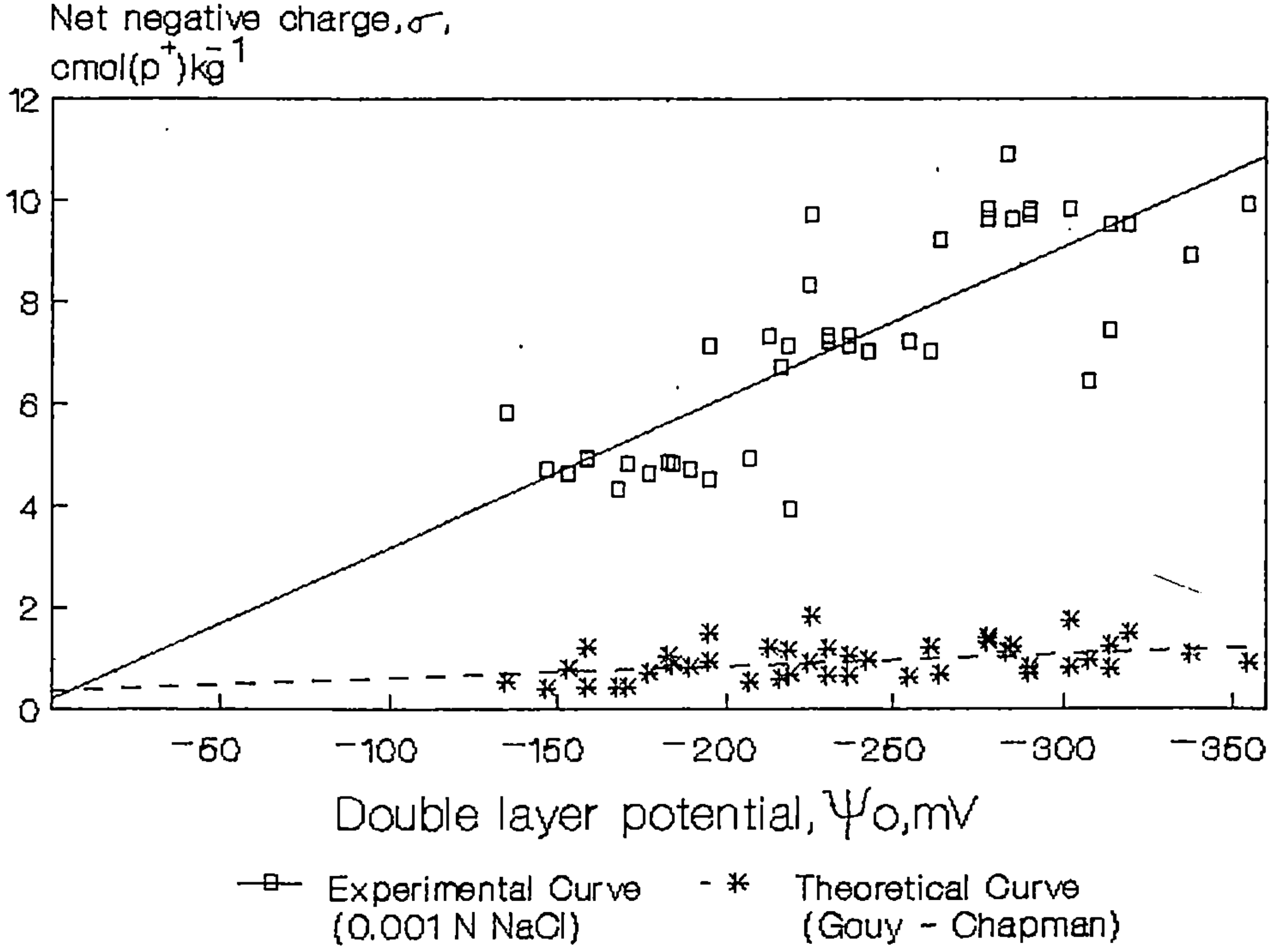


Fig. 19 (b) Experimental and theoretical net negative charge against double layer potential (0.001 N NaCl)



zero point of titration. The maximum shift was by a value of 3.5 cmol (P^+) Kg^{-1} in the case of Haplustult-Ap from Karakulam and the minimum by a value of 1.6 cmol (p^+) Kg^{-1} in the case of the Kandiustult B_2 from Pilicode. The zpc values obtained was invariably lower for the surface samples in all the profiles than the sub-surface. The double layer theory for a reversible interface was employed in the study to predict the variation of electric charge of the soils with pH and electrolyte concentration. Accordingly the net negative surface charge density was calculated as a function of the surface potential and the results are plotted in Fig 18 (a) to 19(b). The surface potential used in making the plots shown was calculated by equation $\psi 0=59$ (zpc-pH) mV at 25°C.

The surface charge used in constructing the curve labelled "Gouy-Chapman" was calculated directly by the Gouy- Chapman equation, after introducing the value of $\psi 0$ given by the above equation.

3. Effect of pH, salt concentration and nature of electrolytes on charge characteristics.

3.1 pH and concentration effect.

The charge distribution of the various soils studied as determined by the four methods of ion adsorption measurement are presented in table 9 and in figure 20 to 27. The results of the statistical analysis of the data is presented in tables 10 to 16. The curves show that positive charges decrease and negative charges increase with increase in pH. A net positive charge was seen in the Kandiustult-B_2 of Pilicode, Paleustult-Bt_2 of Punalur and Haplustox-BA of Pachalloor at pH 3. This effect vanished with a decrease in concentration of the electrolyte.

As pH increased to five all the samples gave negative net charge values. With a decrease in the electrolyte concentration the magnitude of positive and negative net charge decreased. This effect though significant was less pronounced in the case of $CaCl_2$. The concentration effect upon the electric charges were not spectacular as in the case of pH effect mentioned above . Relatively large variation in CEC_T, CEC_B and AEC was observed between pH 4 and 7 in all the four samples studied. CEC_T and CEC_B decreased drastically with decrease in pH from 7 to 4 while significant generation of anion exchange sites was observed at low pH (figures 36 to 39).

Table 9. Variation of electric charges at different p^H values and electrolyte concentrations

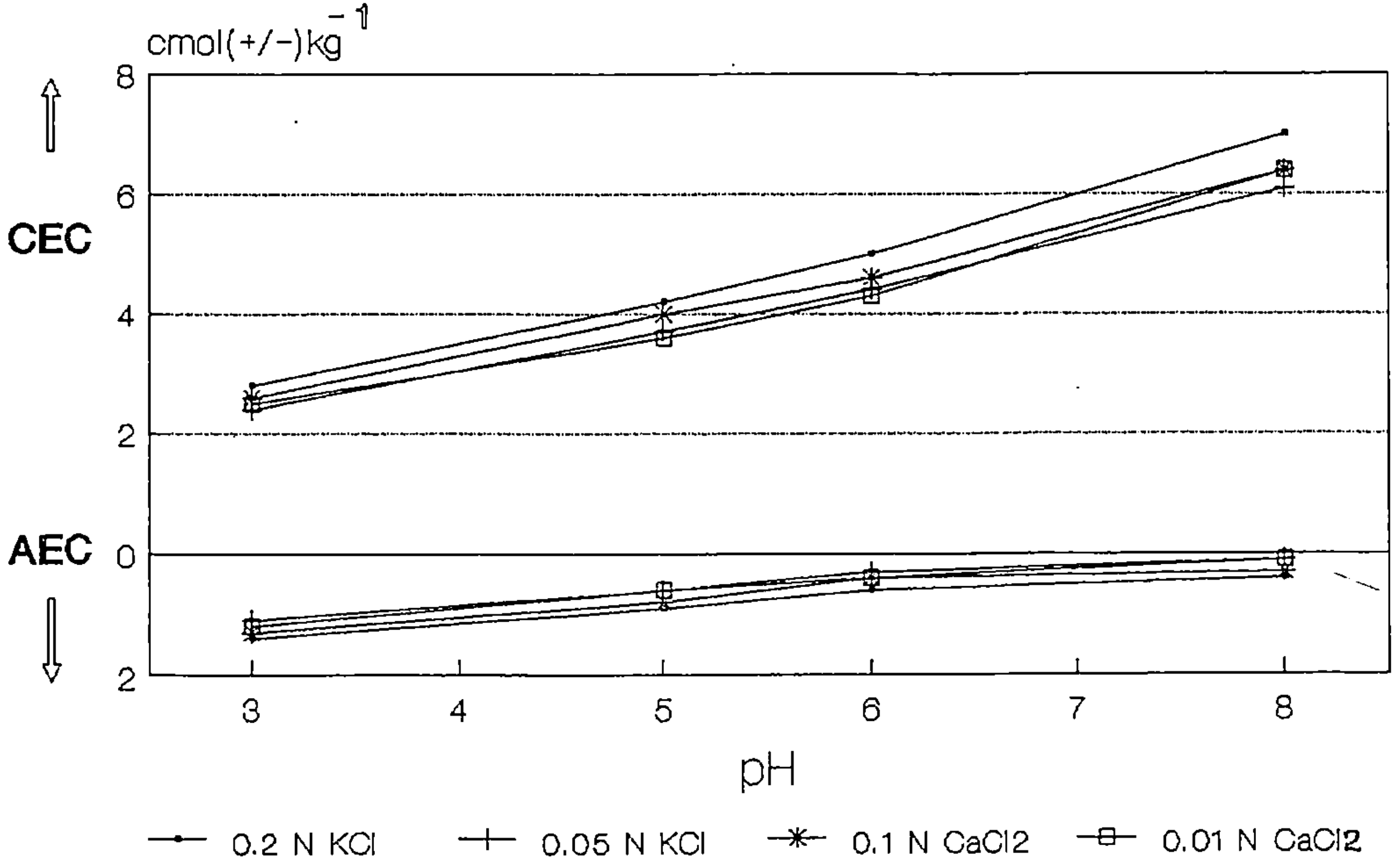
Soil	Horizon	pH	0.2N.KCl (E_1)			0.05 N.KCl (E_2)			0.01N $CaCl_2$ (E_3)			0.01 N $CaCl_2$ (E_4)		
			Neg.	Pos.	Net.	Neg.	Pos.	Net.	Neg.	Pos.	Net.	Neg.	Pos.	Net.
			cmol	(p^+/e)	Kg_{-1}	cmol	(p^+/e)	Kg_{-1}	cmol	(p^+/e)	Kg_{-1}	cmol	(p^+/e)	Kg_{-1}
Kandiustult (Pilicode) (S_1)	Ap	3	2.8	1.4	-1.4	2.4	1.1	-1.3	2.6	1.3	-1.3	2.5	1.2	-1.3
		5	4.2	0.9	-3.3	3.7	0.6	-3.1	4.0	0.8	-3.2	3.6	0.6	-3.0
		6	5.0	0.6	-4.4	4.4	0.3	-4.1	4.6	0.4	-4.2	4.3	0.4	-3.9
		8	7.0	0.4	-6.6	6.1	0.1	-6.0	6.4	0.3	-6.1	6.4	0.1	-6.3
Kandiustult (Pilicode) (S_2)	B_2	3	2.0	2.4	+0.4	1.8	2.0	+0.2	1.8	1.9	+0.1	1.6	1.6	0.0
		5	2.2	2.1	-0.1	2.1	1.6	-0.4	2.1	2.0	-0.1	2.1	1.6	-0.5
		6	3.1	1.6	-1.5	2.6	1.2	-1.4	2.6	1.4	-1.2	2.4	1.2	-1.2
		8	4.8	0.9	-3.7	3.2	0.3	-2.9	4.4	0.7	-3.7	4.1	0.6	-3.5
Plinthustuit (Pilathara) (S_3)	Ap	3	4.2	2.1	-2.1	3.4	1.6	-1.8	4.0	2.0	-2.0	4.4	1.6	-3.4
		5	5.8	1.2	-4.6	4.9	1.0	-3.9	5.2	1.0	-4.2	4.8	0.8	-4.0
		6	6.4	0.6	-5.8	5.4	0.2	-5.2	6.0	0.4	-5.6	5.3	0.2	-5.1
		8	7.8	0.2	-7.6	6.1	0.2	95.9	7.2	0.2	-7.0	6.4	0.2	-6.2
Plinthustuit (Pilathara) (S_4)	B_{21}	3	2.9	1.6	-1.3	2.3	1.2	-1.1	2.6	1.5	-1.1	2.5	1.3	-1.2
		5	3.7	1.3	-2.4	3.1	0.9	-2.2	3.5	1.2	-2.3	3.4	1.0	-2.4
		6	4.4	0.6	-3.8	3.8	0.3	-3.5	4.1	0.4	-3.7	4.0	0.2	-3.8
		8	5.9	0.1	-5.8	4.9	0.0	-4.9	5.6	0.2	-5.4	5.2	0.2	-5.0

(Contd.)

Table 9. Variation of electric charges at different p^H values and electrolyte concentrations (Contd.)

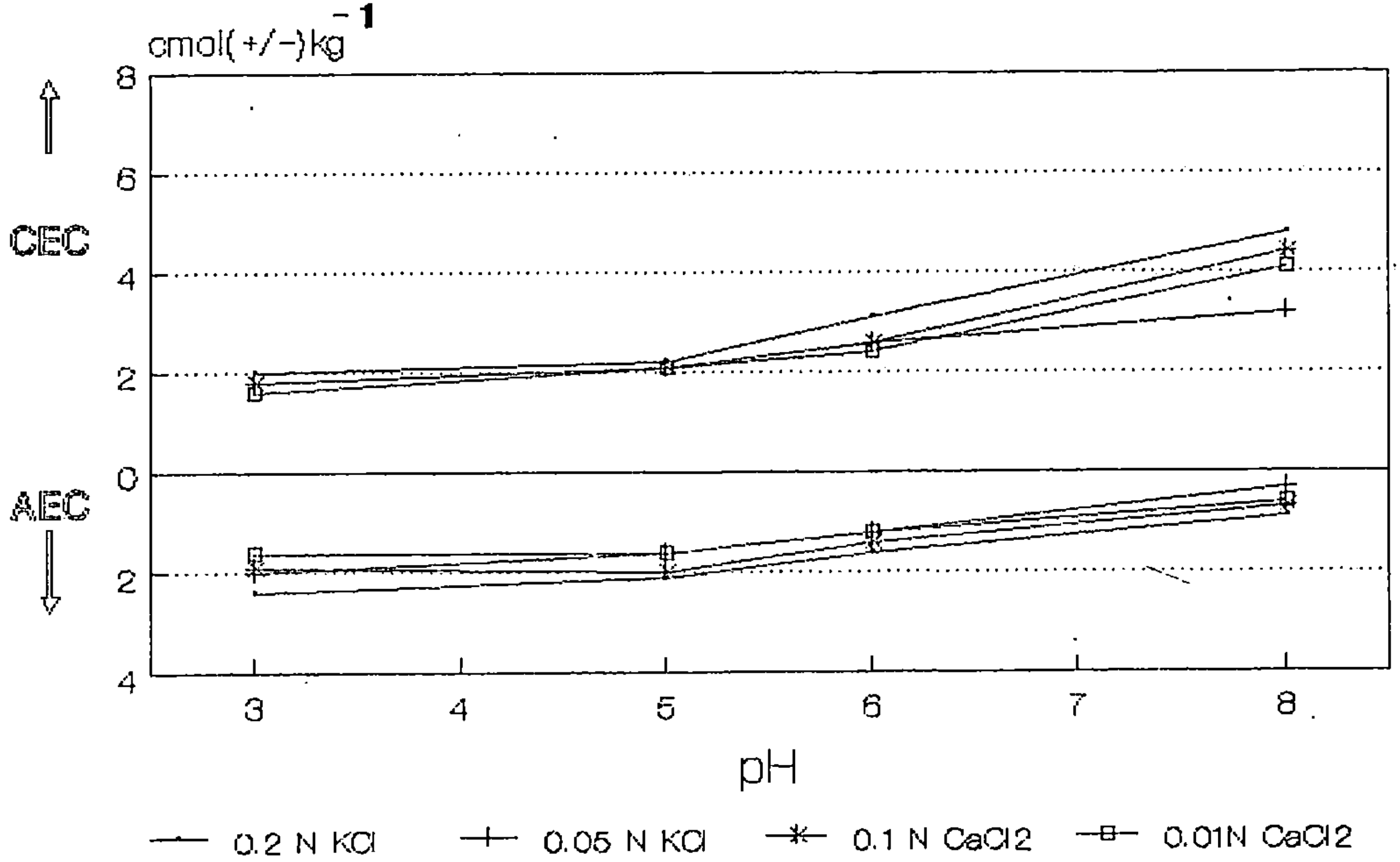
Soil	Horizon	pH	0.2N.KCl (E_1)			0.05 N.KCl (E_2)			0.01N $CaCl_2$ (E_3)			0.01 N $CaCl_2$ (E_4)		
			Neg.	Pos.	Net.	Neg.	Pos.	Net.	Neg.	Pos.	Net.	Neg.	Pos.	Net.
			cmol	(p^+/e)	Kg$_{-1}$	cmol	(p^+/e)	Kg$_{-1}$	cmol	(p^+/e)	Kg$_{-1}$	cmol	(p^+/e)	Kg$_{-1}$
Paleustult		3	3.3	1.2	-2.1	2.9	1.2	-1.7	3.2	1.2	-2.0	3.8	1.4	-2.4
(Punalur)	(S_5) A_1	5	6.8	0.9	-5.8	5.9	0.6	-5.3	6.1	0.8	-5.3	5.3	0.6	-4.7
		6	7.5	0.4	-7.1	6.2	0.2	-6.0	6.6	0.5	-6.1	5.9	0.4	-5.5
		8	7.8	0.2	-7.6	6.8	0.0	-6.8	7.3	0.2	-7.1	6.4	0.1	-6.3
Paleustult		3	2.2	2.6	+0.4	2.1	2.4	+0.3	1.8	2.4	+0.6	1.8	2.1	+0.3
(Punalur)	(S6)Bt_2	5	2.6	2.4	-0.2	2.5	2.0	-0.5	2.3	2.1	-0.2	2.1	1.6	-0.5
		6	3.5	1.2	-2.3	3.5	1.1	-2.4	2.6	0.6	-2.0	2.9	0.8	-2.1
		8	4.4	0.4	-4.0	4.2	0.2	-4.0	3.8	0.2	-3.6	3.6	0.2	-3.4
Haplustox		3	3.3	2.8	-0.5	3.2	2.3	-0.9	3.4	2.6	-0.8	3.1	2.4	-0.7
(Pachalloor)	(S_7)Ap	5	4.3	2.2	-2.1	4.0	2.0	-2.0	4.1	2.0	-2.1	3.6	1.8	-1.8
		6	4.8	0.6	-4.2	4.8	0.8	-4.0	4.8	0.6	-4.2	4.2	1.0	-3.2
		8	5.4	0.2	-5.2	5.2	0.2	-5.0	5.9	0.2	-5.7	4.9	0.2	-4.7
Haplustox		3	2.4	3.1	+0.7	2.4	2.2	-0.2	1.4	2.5	+1.1	1.8	2.2	+0.4
(Pachalloor)	(S_8)BA	5	3.1	2.4	-0.7	2.9	0.8	-2.1	2.4	2.3	-0.1	2.2	1.8	-0.4
		6	4.8	1.6	-3.2	4.1	0.2	-3.9	3.6	0.8	-2.8	3.2	0.9	-2.3
		8	5.6	0.4	-5.2	4.8	0.2	-4.6	4.9	0.2	-4.7	4.8	0.2	-4.6

Fig. 20 : Variation of positive and negative charges as a function of pH and electrolyte concentration



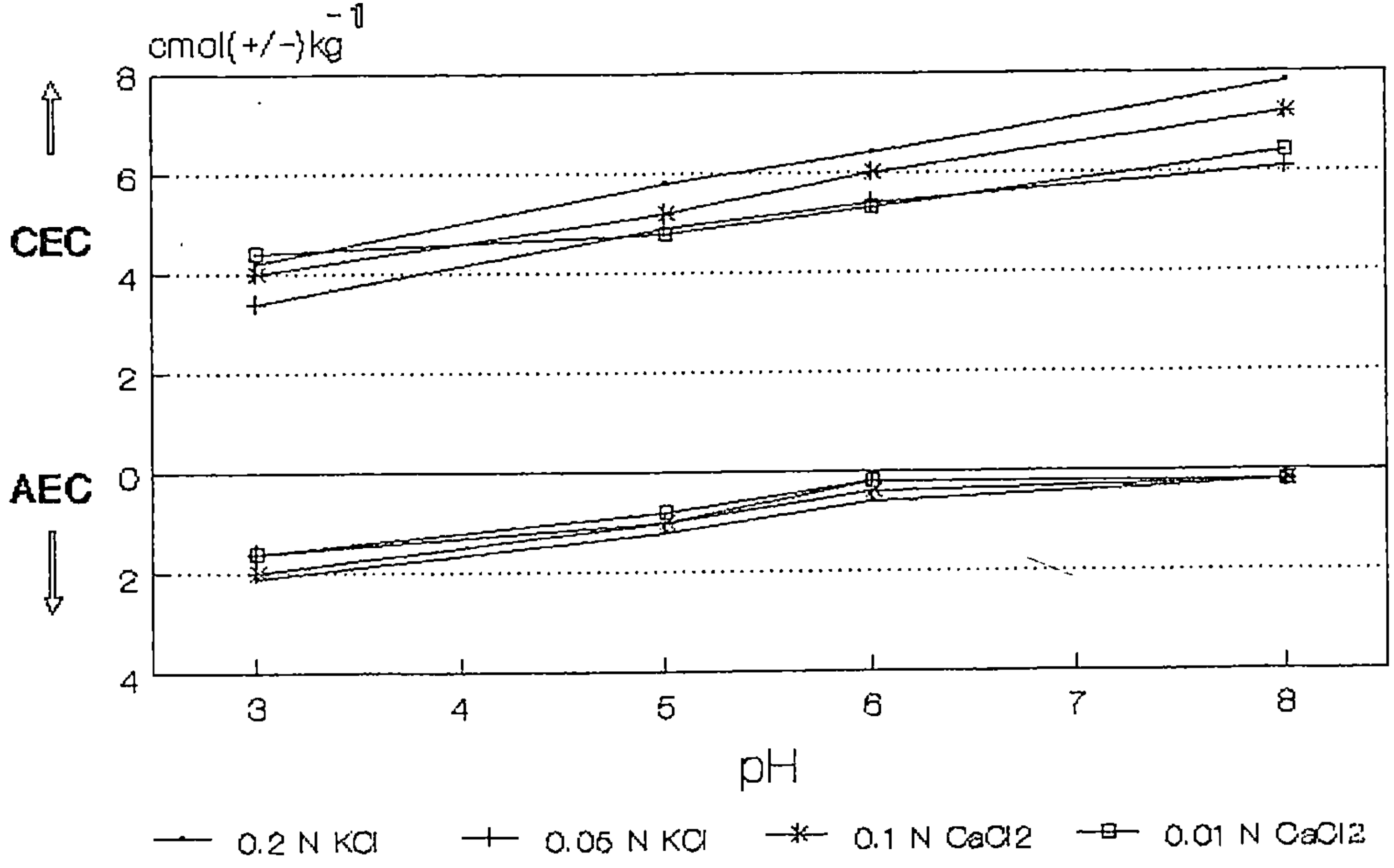
KANDIUSTULT - Ap (Pilicode)

Fig. 21 : Variation of positive and negative charges as a function of pH and electrolyte concentration



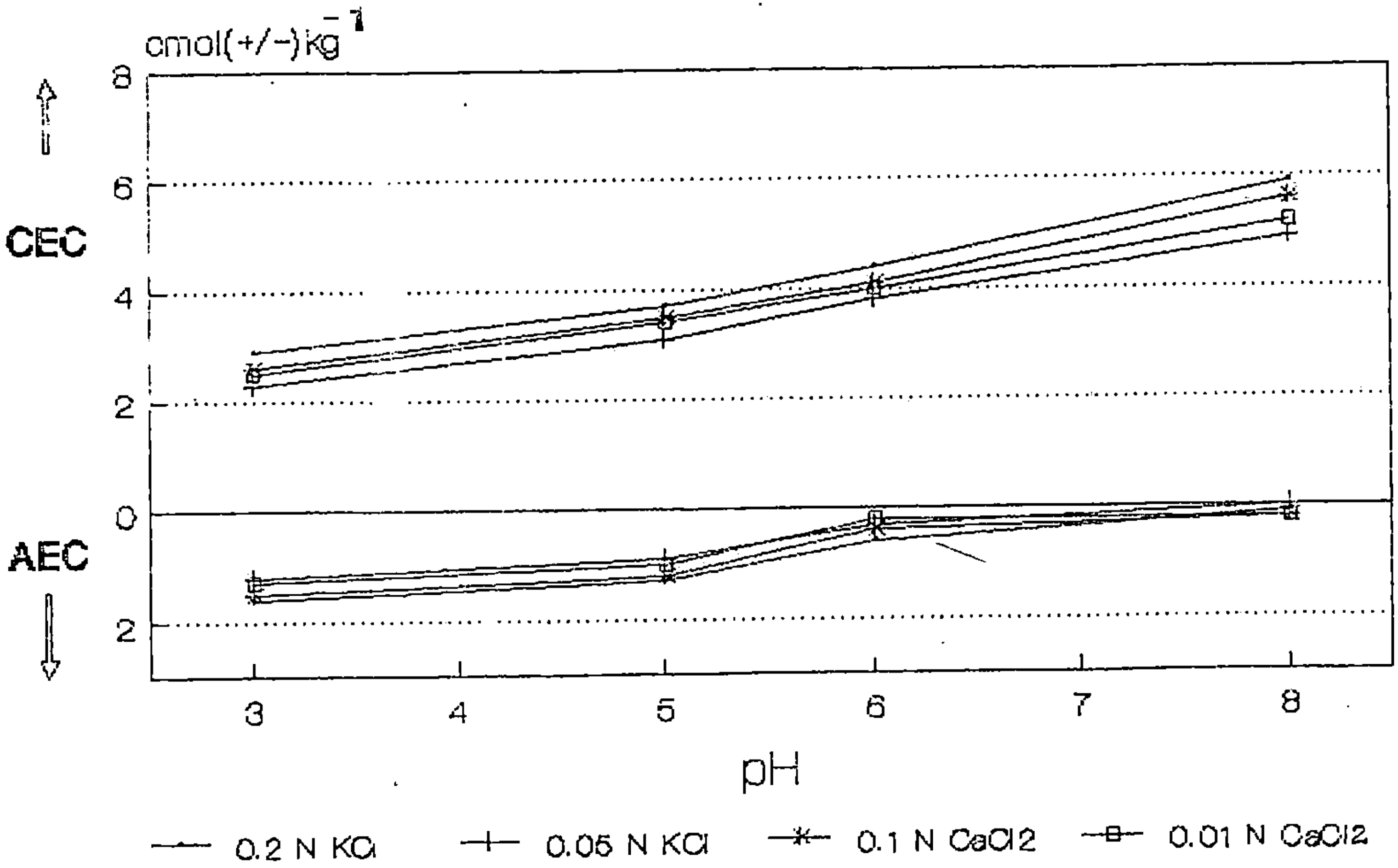
KANDIUSTULT - B2 (Pilicode)

Fig. 22 : Variation of positive and negative charges as a function of pH and electrolyte concentration



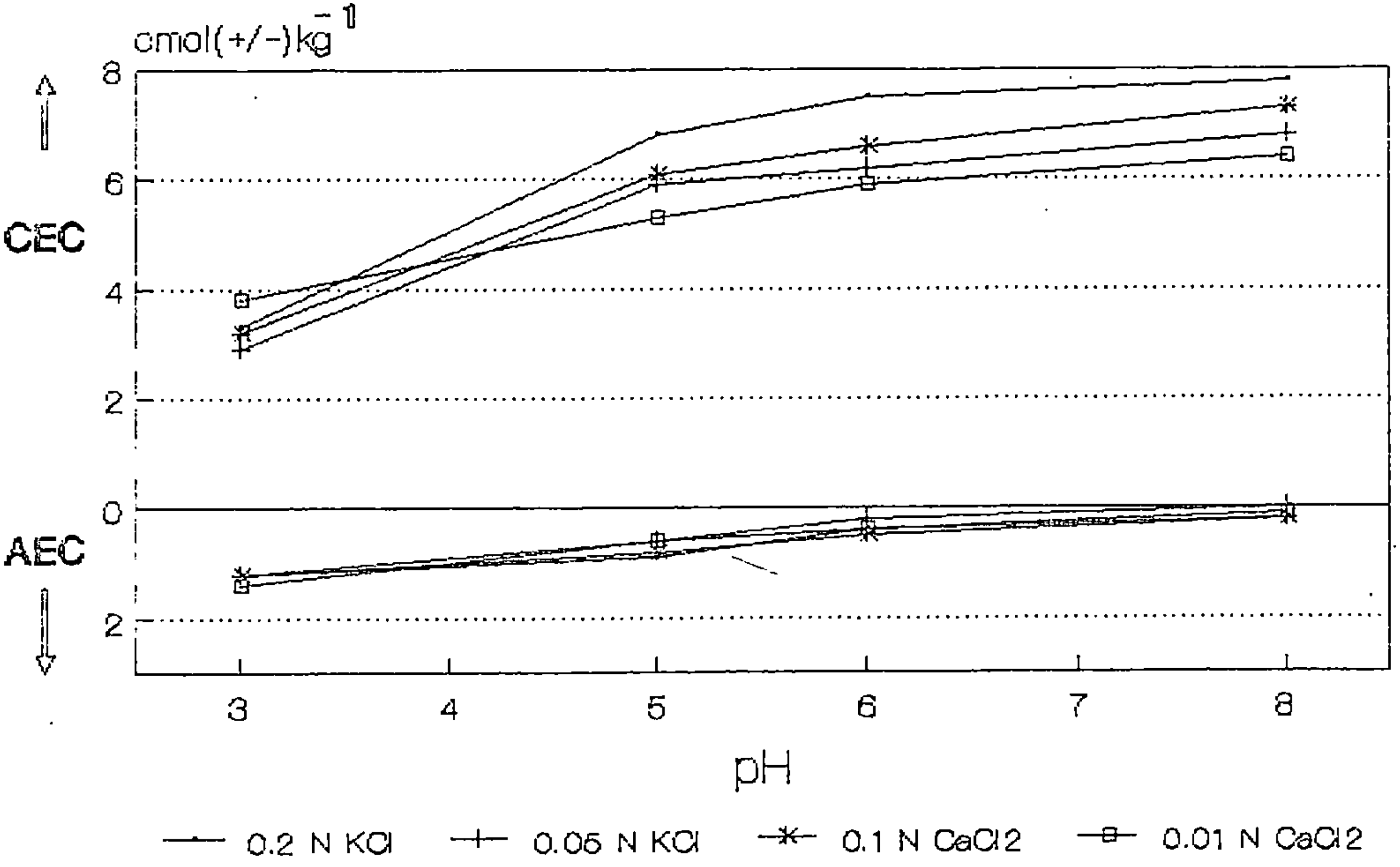
PLINTHUSTULT - Ap (Pilathara)

Fig. 23 : Variation of positive and negative charges as a function of pH and electrolyte concentration



PLINTHUSTULT - B21 (Pilathara)

Fig. 24 : Variation of positive and negative charges as a function of pH and electrolyte concentration



PALEUSTULT - A1 (Punalur)

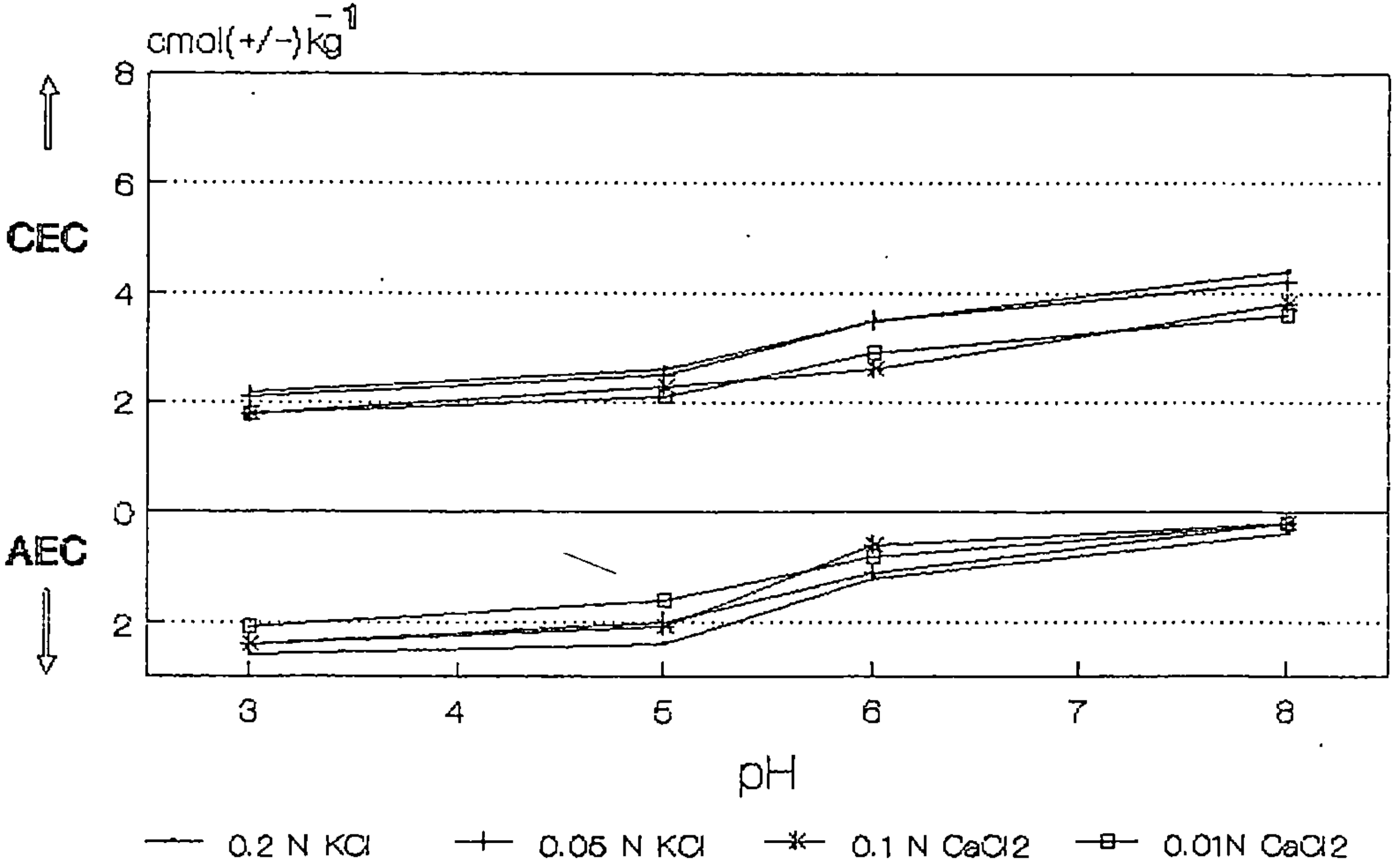
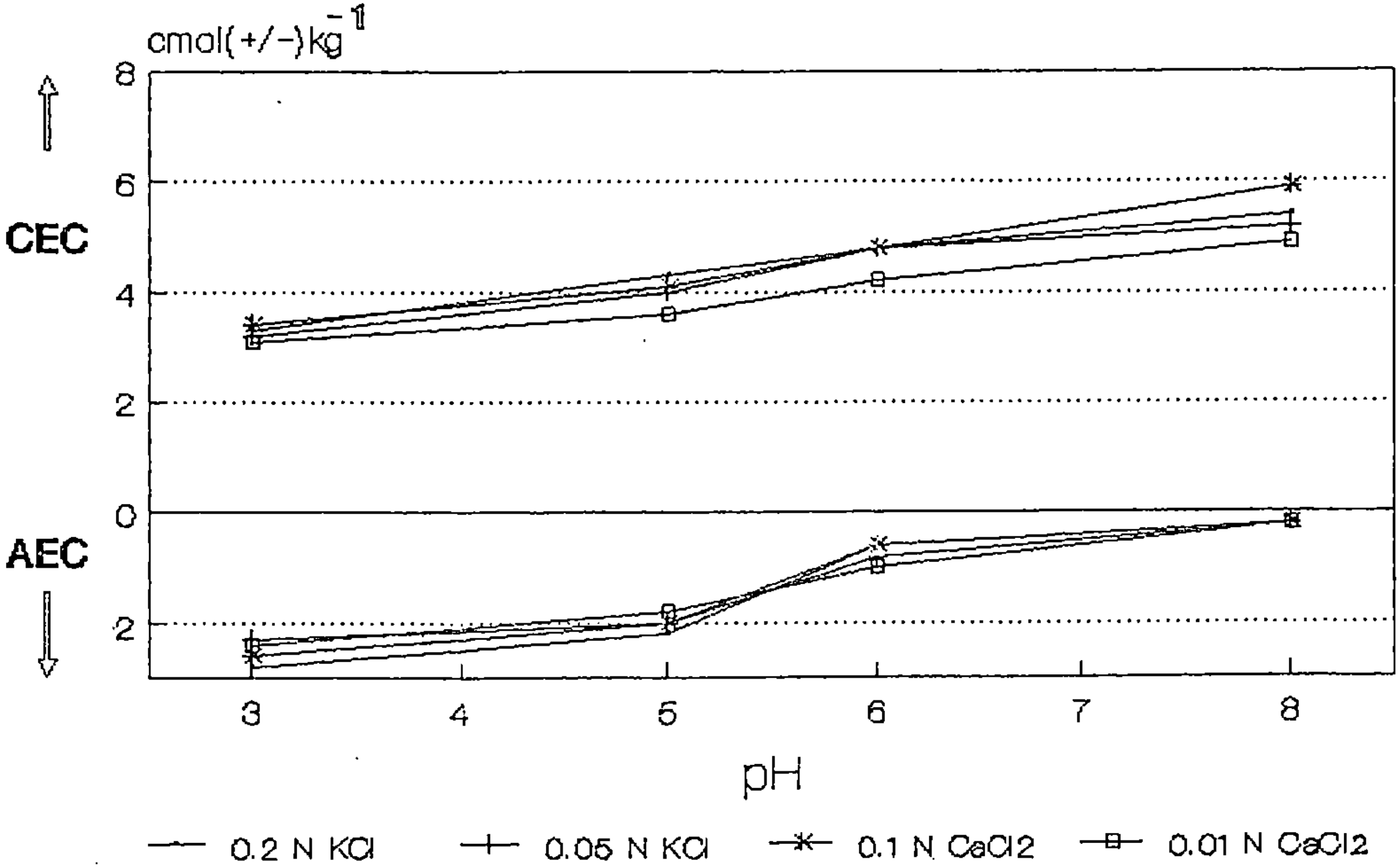


Fig. 25 : Variation of positive and negative charges as a function of pH and electrolyte concentration

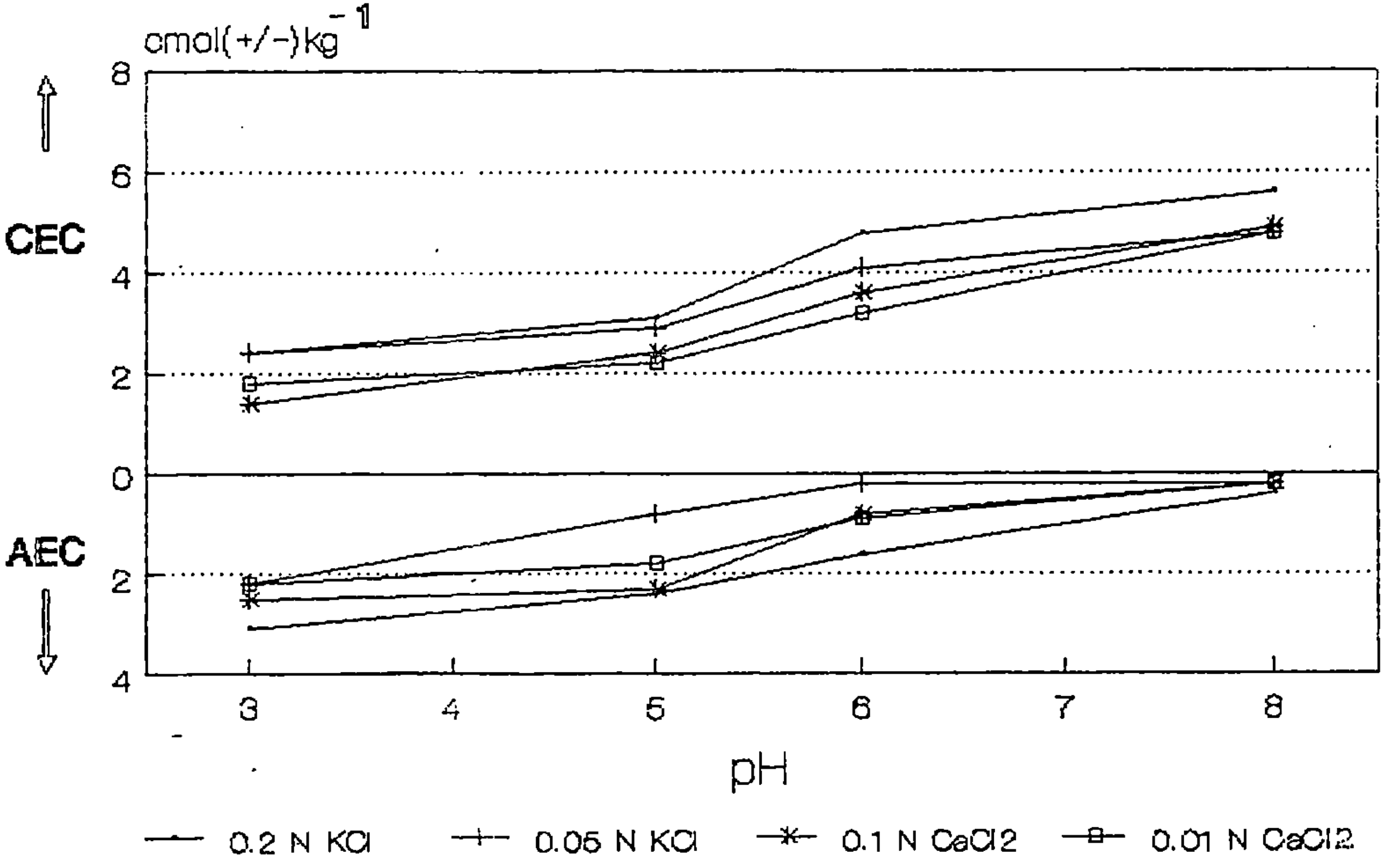
PALEUSTULT - Bt2 (Punalur)

Fig. 26 : Variation of positive and negative charges as a function of pH and electrolyte concentration



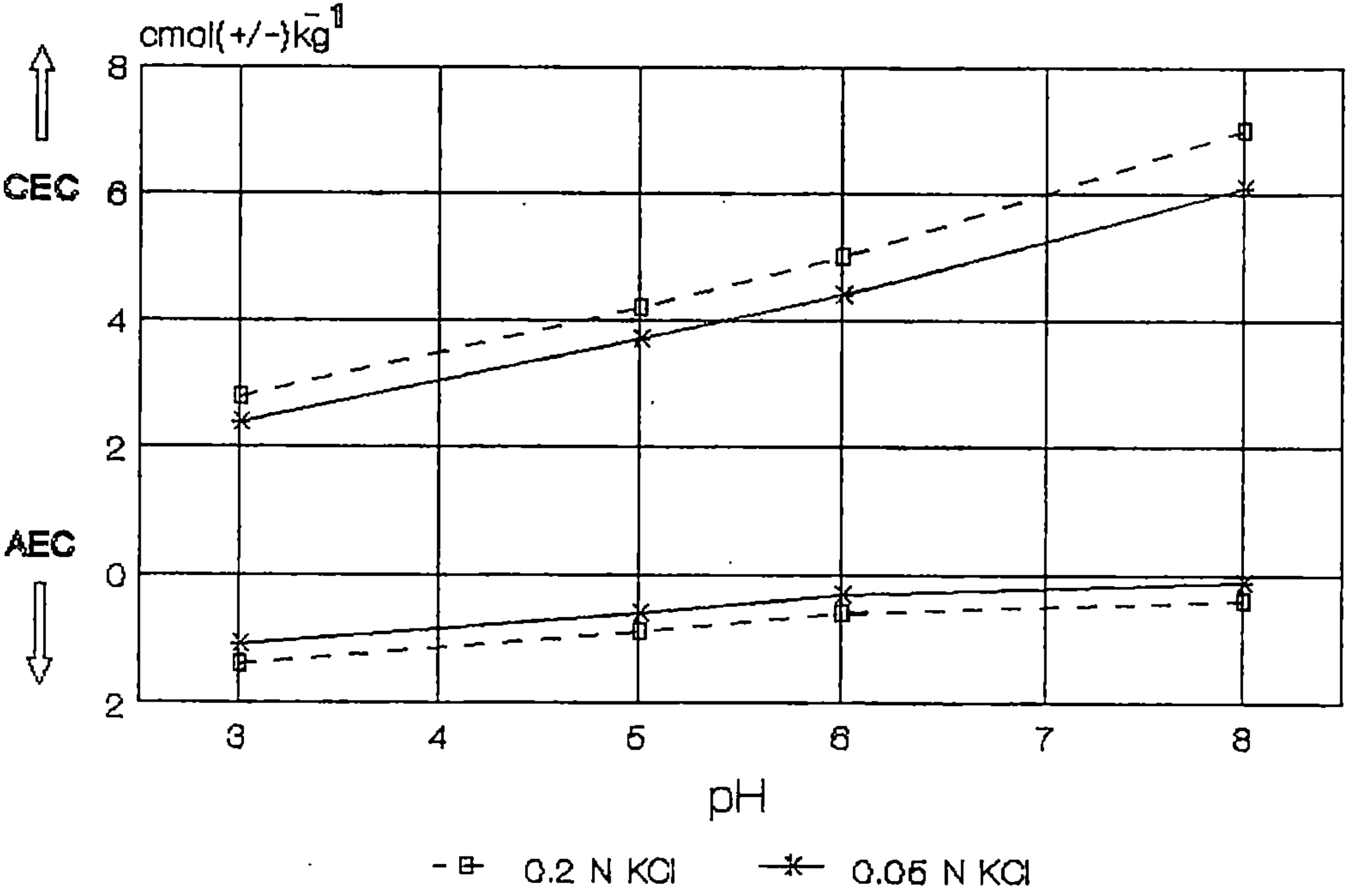
HAPLUSTOX - Ap (Pachalloor)

Fig. 27 : Variation of positive and negative charges as a function of pH and electrolyte concentration



HAPLUSTOX - BA (Pachalloor)

Fig. 28: Curves of CEC and AEC versus pH measured in two concentrations of KCl



KANDIUSTULT - Ap (Pilicode)

Fig. 29: Curves of CEC and AEC versus pH measured in two concentrations of KCl

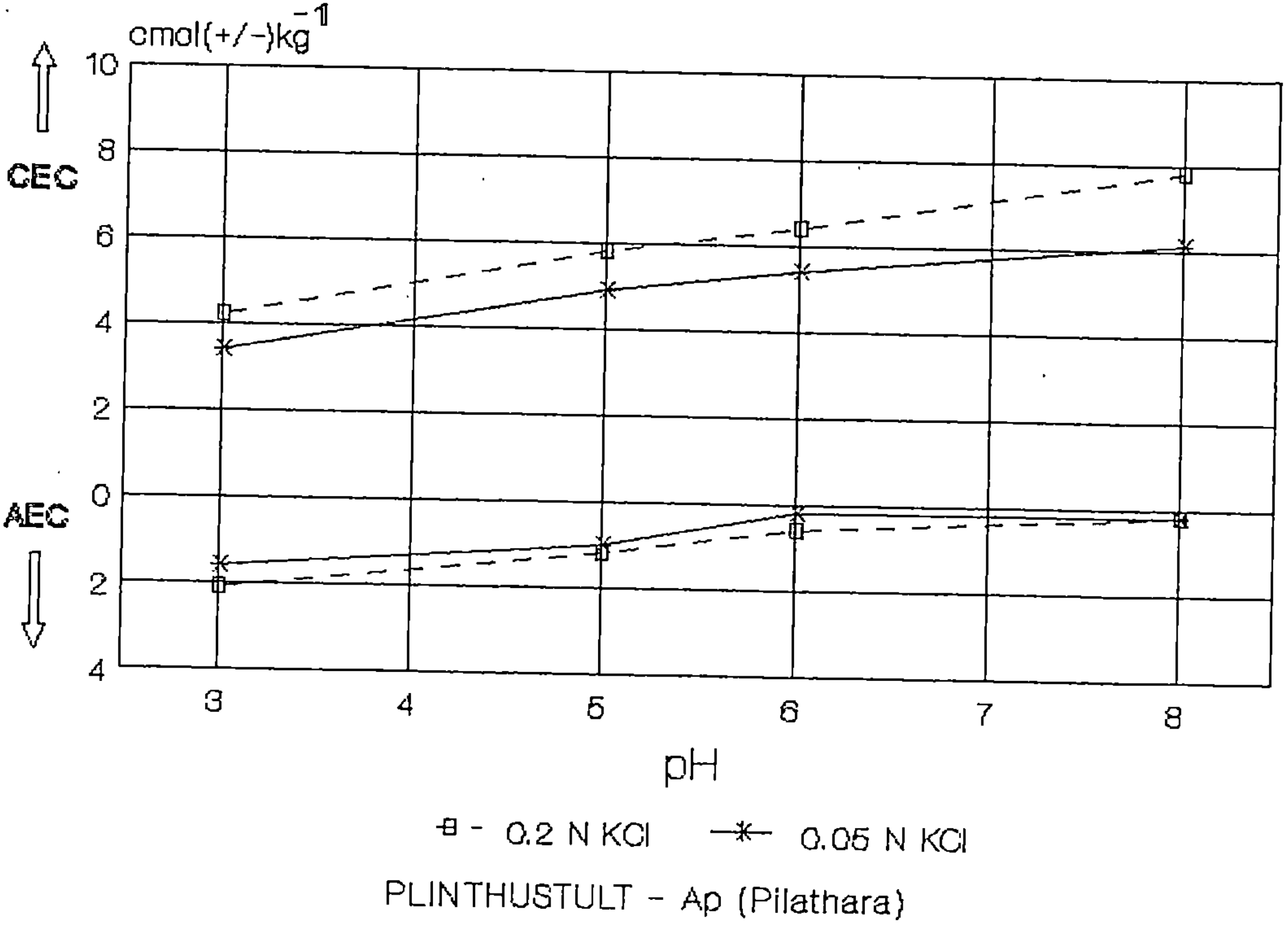
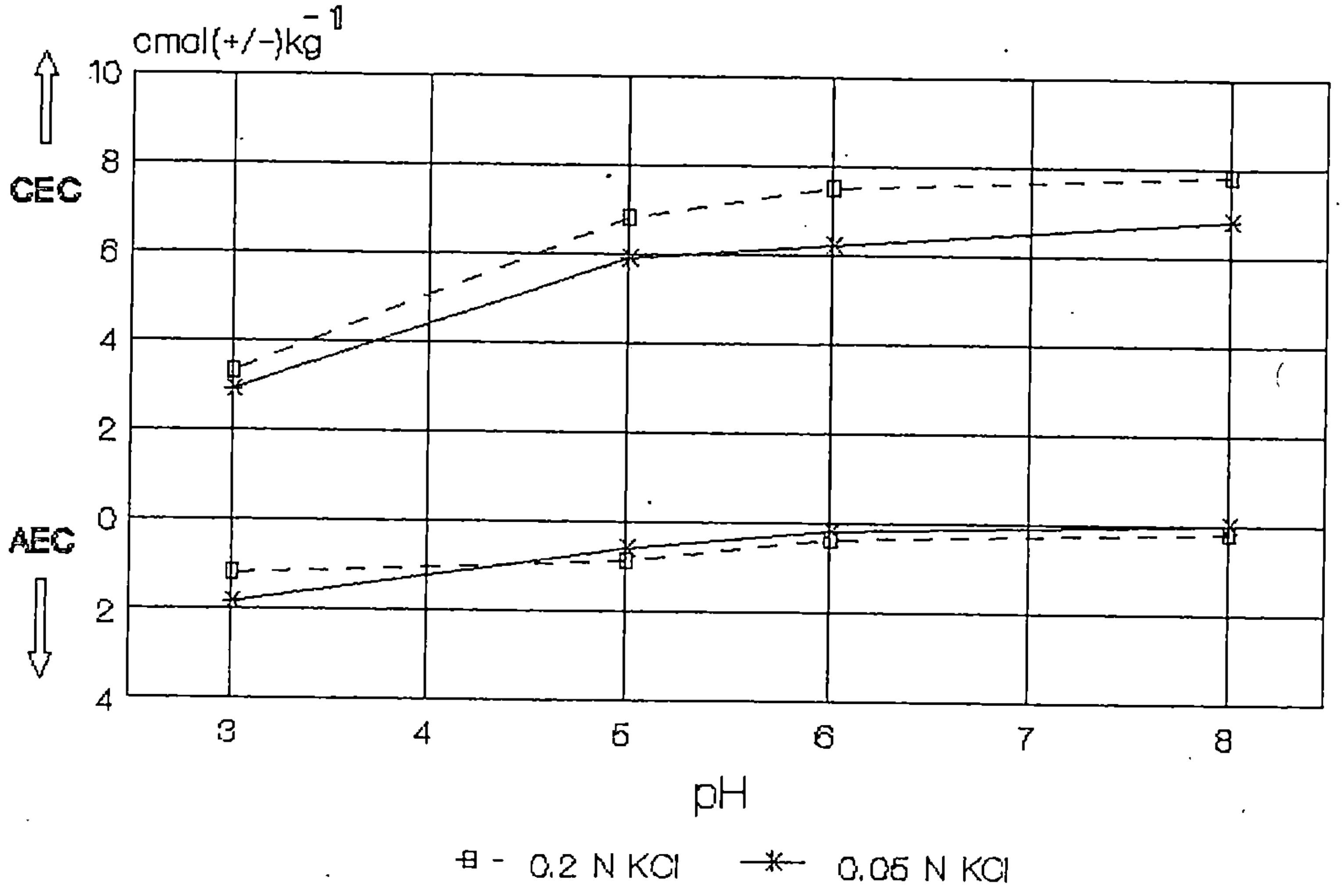


Fig. 30: Curves of CEC and AEC versus pH measured in two concentrations of KCl



PALEUSTULT - A1 (Punalur)

Fig. 31: Curves of CEC and AEC versus pH measured in two concentrations of KCl

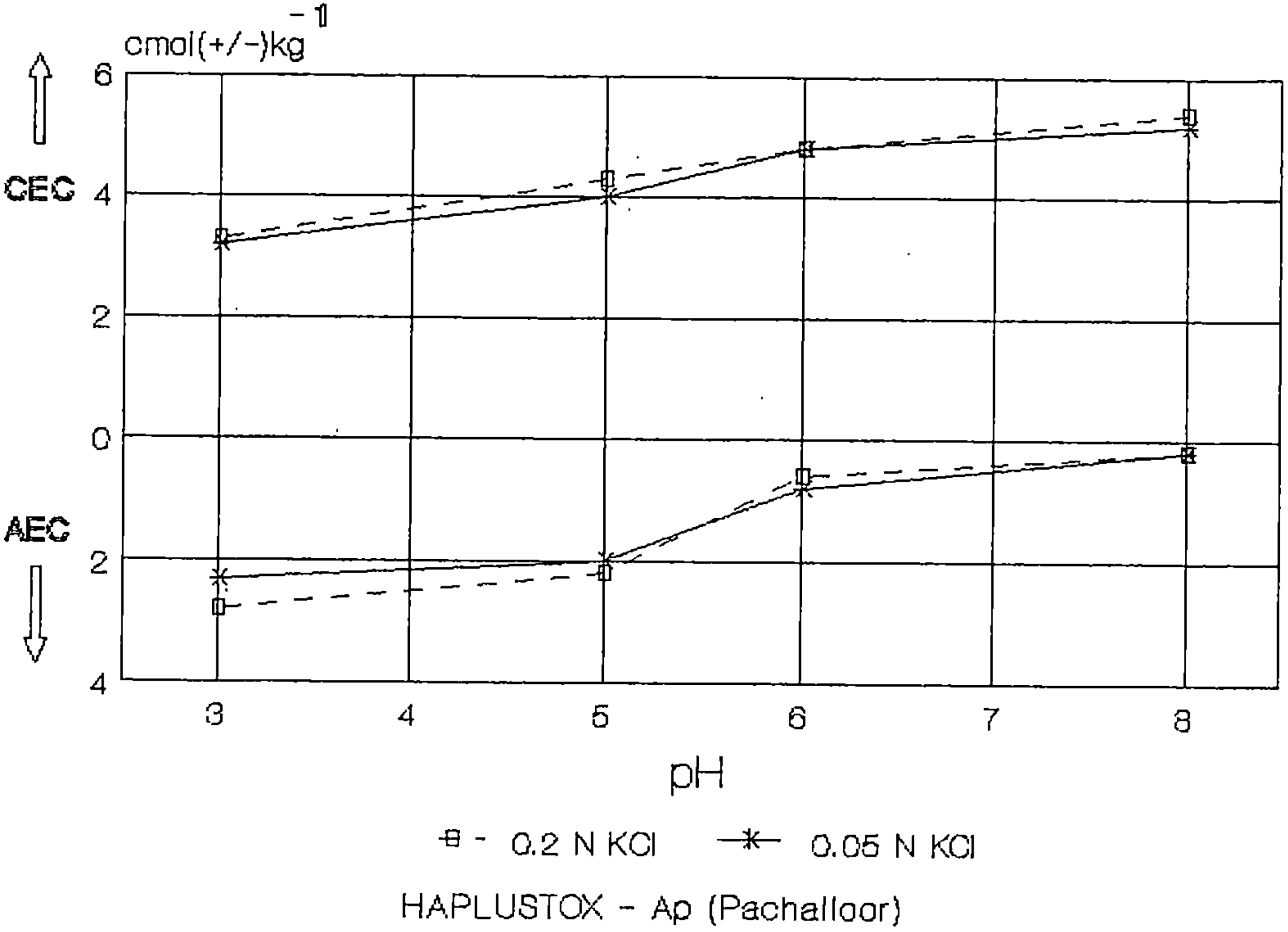


Fig. 32: Curves of CEC and AEC versus pH measured in two concentrations of $CaCl_2$

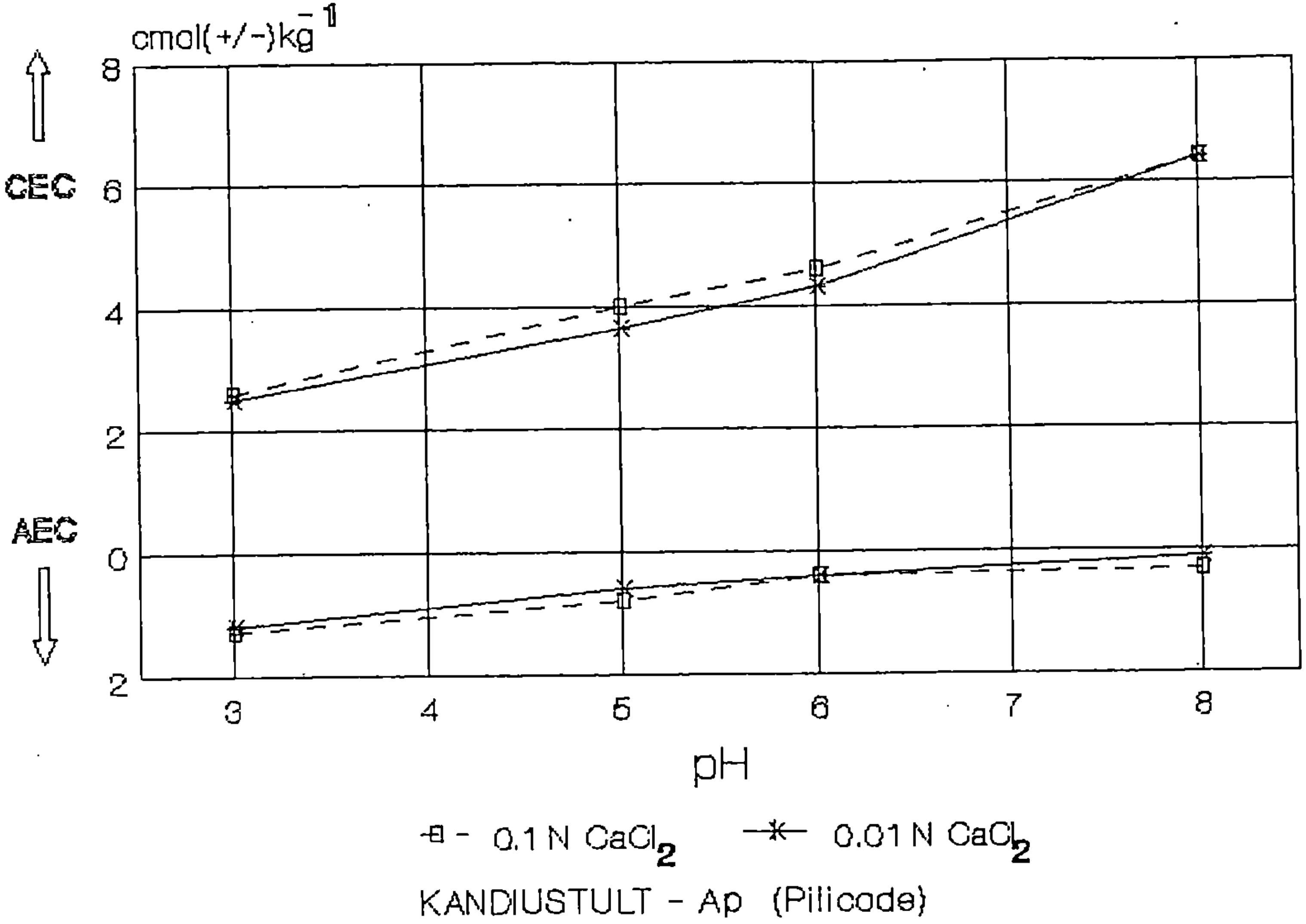


Fig. 33: Curves of CEC and AEC versus pH measured in two concentrations of $CaCl_2$

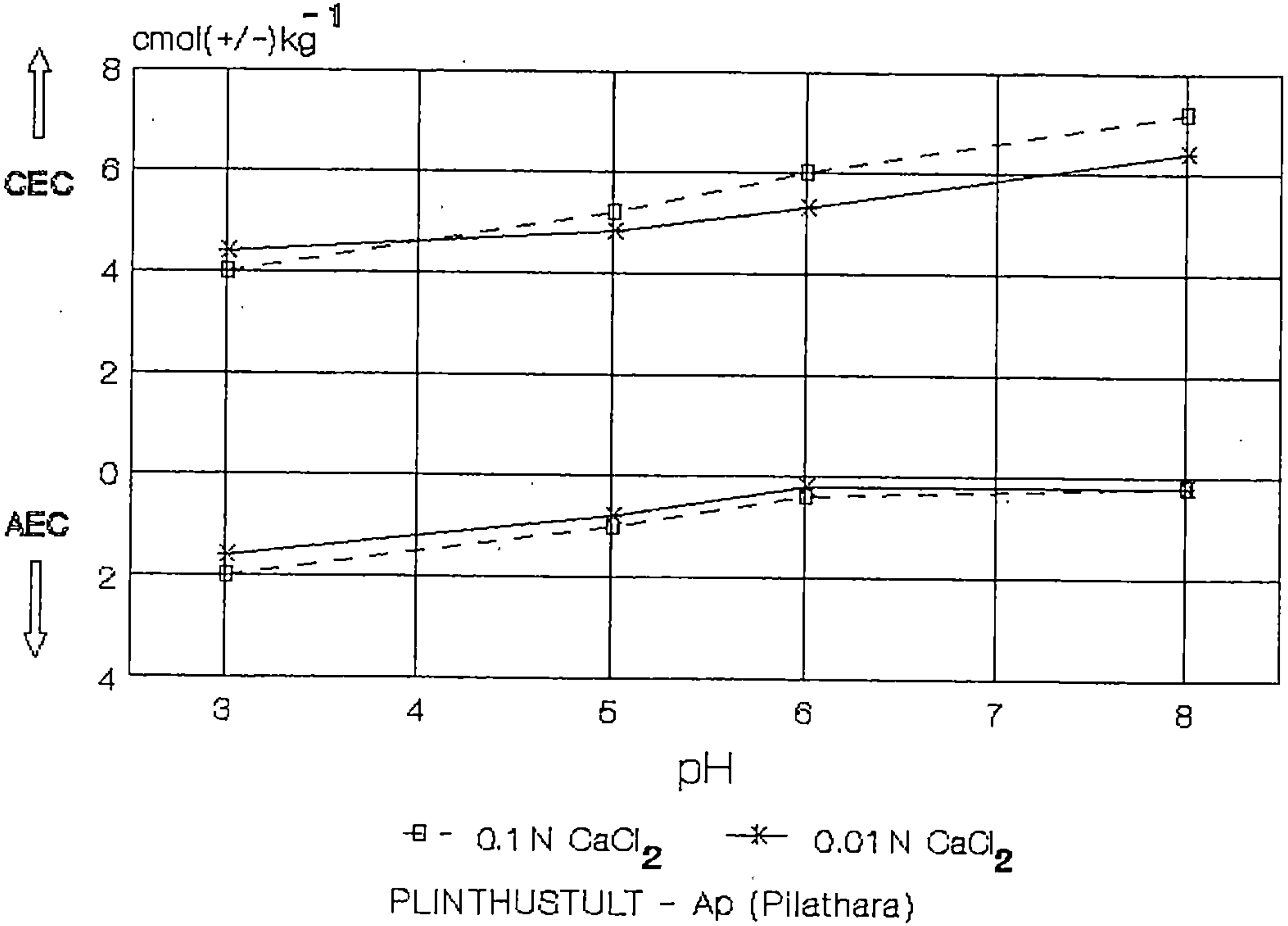


Fig. 34: Curves of CEC and AEC versus pH measured in two concentrations of $CaCl_2$

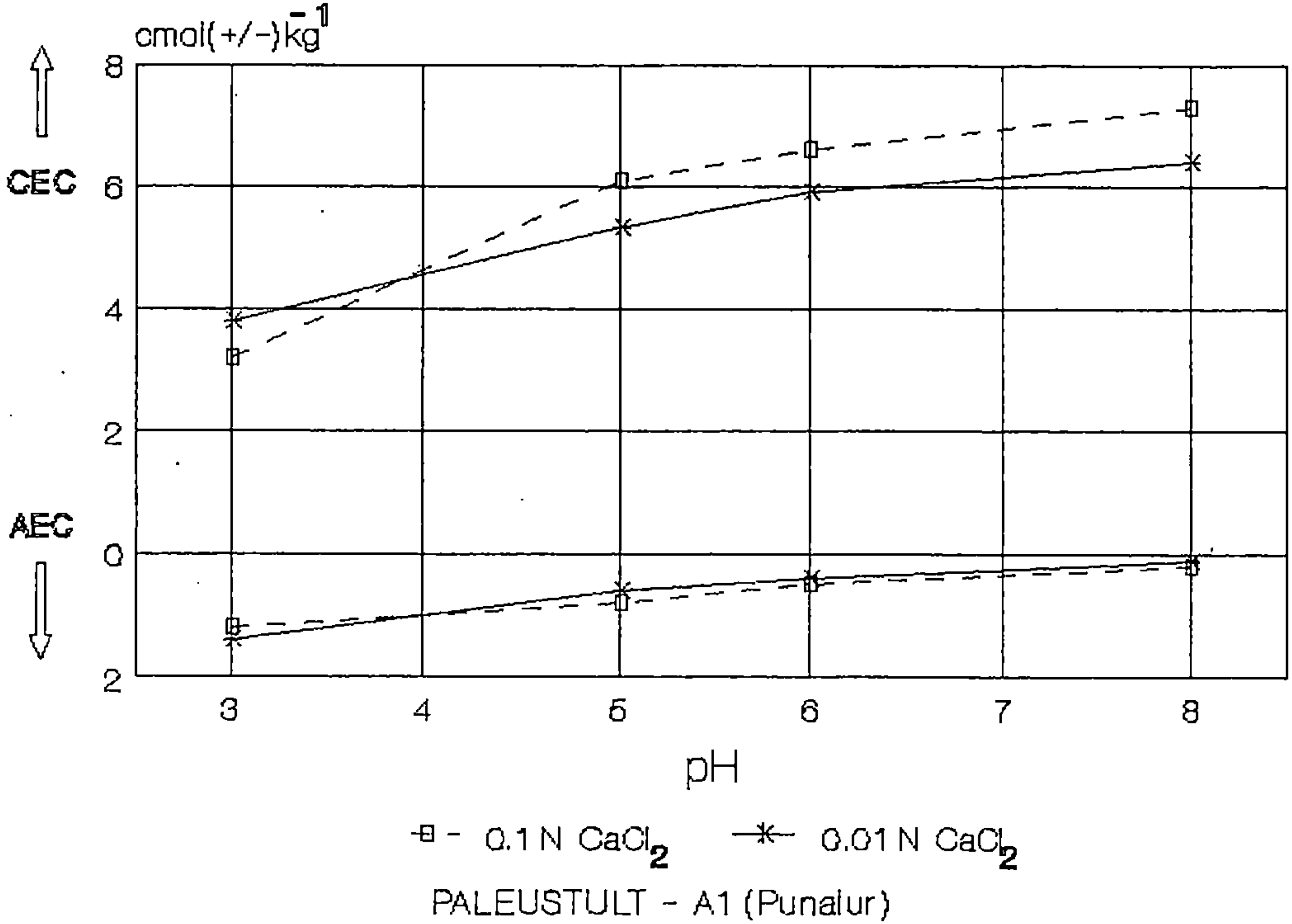
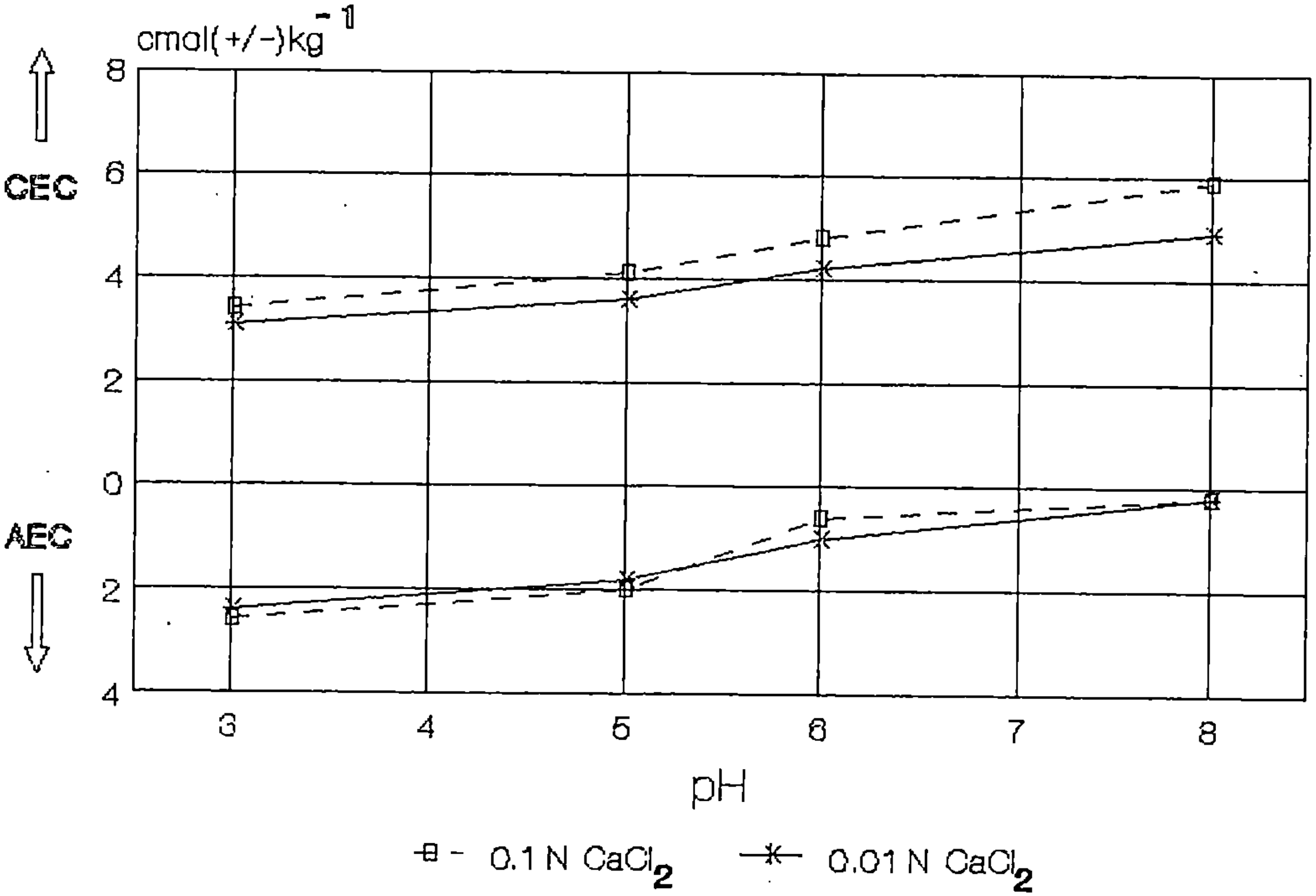


Fig. 35: Curves of CEC and AEC versus pH measured in two concentrations of $CaCl_2$



HAPLUSTOX - Ap (Pachalloor)

Table 10. CEC as influenced by different electrolytes in different soils at different pH values.

Electrolytes.	Soils								pH			
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	pH_3	pH_5	pH_6	pH_8
E_1	4.75	3.02	6.05	4.22	6.35	3.17	4.45	3.98	2.88	4.08	494	6.08
E_2	4.15	2.42	4.95	3.52	5.45	3.07	4.30	3.55	2.56	3.63	4.35	5.16
E_3	4.40	2.72	5.60	3.95	5.80	2.62	4.55	3.07	2.60	3.71	4.36	5.69
E_4	4.20	2.55	5.22	3.77	5.35	2.60	3.95	3.00	2.69	3.39	4.03	5.23

pH								
pH_3	2.57	1.80	4.00	2.57	3.30	1.98	3.25	2.00
pH_5	3.88	2.12	5.17	3.42	6.02	2.37	4.00	2.65
pH_6	4.57	2.68	5.78	4.08	6.55	3.13	4.65	3.93
pH_8	6.48	4.13	6.88	5.40	7.08	4.00	5.35	5.03

CD (0.05) E = 0.107

CD (0.05) S = 0.152

CD (0.05) pH = 0.107

CD (0.05) ExS = 0.303

CD (0.05) ExpH = 0.215

CD (0.05) SxpH = 0.303

F (E) = 60.53
F (S) = 432.57
F (pH) = 1004.49

F (ExS) = 4.07
F (ExpH) = 5.12
F (SxpH) = 15.37

3.2 The Electrolyte effect

At lower pH values higher concentration of monovalent electrolyte gave higher estimates of CEC. The same was true for AEC also. When pH was 3, highest dose of KCl gave maximum CEC values and the lowest dose of $CaCl_2$ was equally effective. No significant differences in CEC was seen at the two levels of $CaCl_2$ (figures 32 to 35). At the highest pH level the lowest dose of both the electrolytes was equally effective, the maximum being estimated by $CaCl_2$. At higher pH, KCl recorded maximum CEC values (figures 28 to 31). For AEC measurements the effect of electrolyte concentration was not much pronounced as in CEC since the anion is the same though the individual and interaction effects were significant. The effect of associatied cation and concentration was not reflected in the case of AEC.

The analysis of variance showed significant effect due to pH and electrolyte concentration on the estimated values of CEC and AEC. Although the differences in the electric charge was chiefly pH and concentration dependant, the analysis of variance had revealed significant effects due to soils too. The interactions, Soil x Electrolyte, Soil x pH and Electrolyte x pH were all highly significant for both AEC and CEC estimations. The results are presented in tables 10 to 15. The effects of the various components of variation were tested against the highest order interaction.

4. Evaluation of methods of ion-exchange measurements.

The data on ion-exchange measurements studied by different methods are summarised in Table 17. The analysis of variance data presented in Table 18 showed significant effects due to various methods of ion exchange determinations. Values obtained for CEC determinations by the ammonium acetate method and ECEC were higher compared to the other methods. Taking compulsive exchange as the standard method no significant differences were observed for K-exchange from KCl, Na^+ exchange from NaCl, CEC_T and CEC_B.

Among anion exchange measurements, there was no significant difference between compulsive exchange and Cl^- exchange from $CaCl_2$. Chloride exchange from NaCl, also gave comparable values but was significantly different from compulsive exchange method. However NaCl and $CaCl_2$ methods were not significant statistically.

5. Characterization of permanent and pH dependant charge

The values of permanent charge determined by different methods are presented in Table 19. Permanent charge determined were negative in all the samples used. Permanent charge measured by K^+ and Cl^- adsorption method as outlined by

Fig. 36 : Curves of CEC_B CEC_T and AEC versus pH

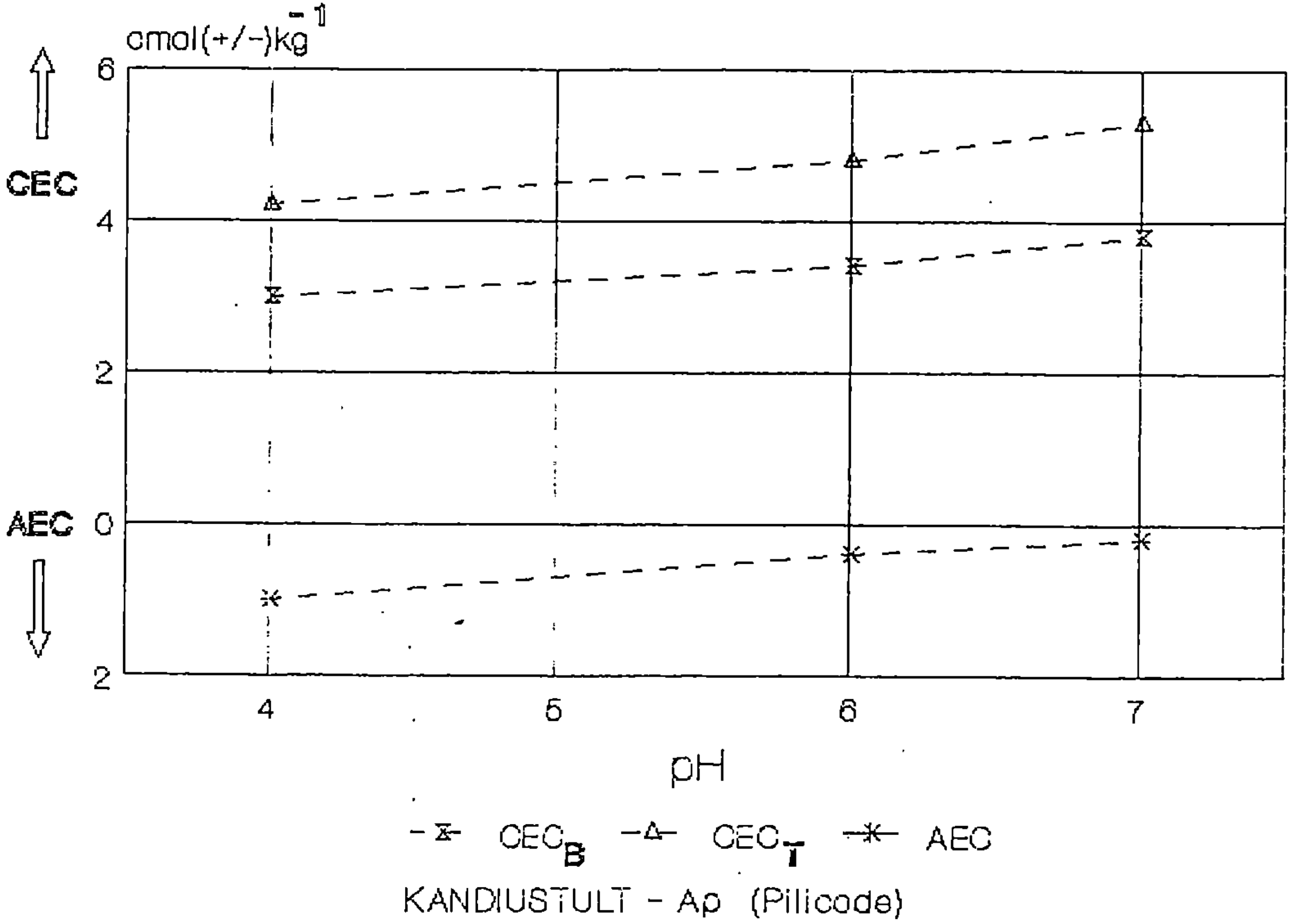
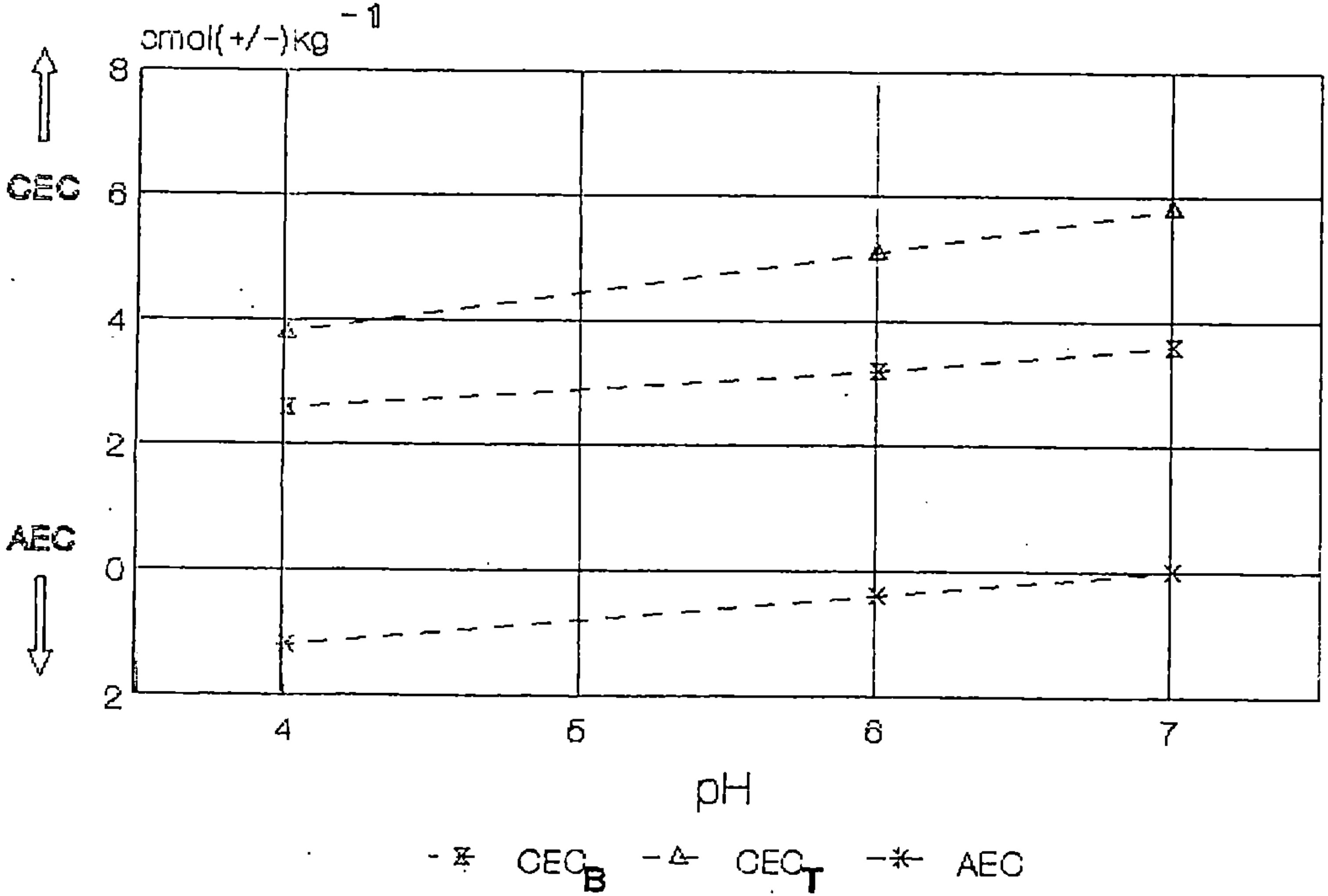
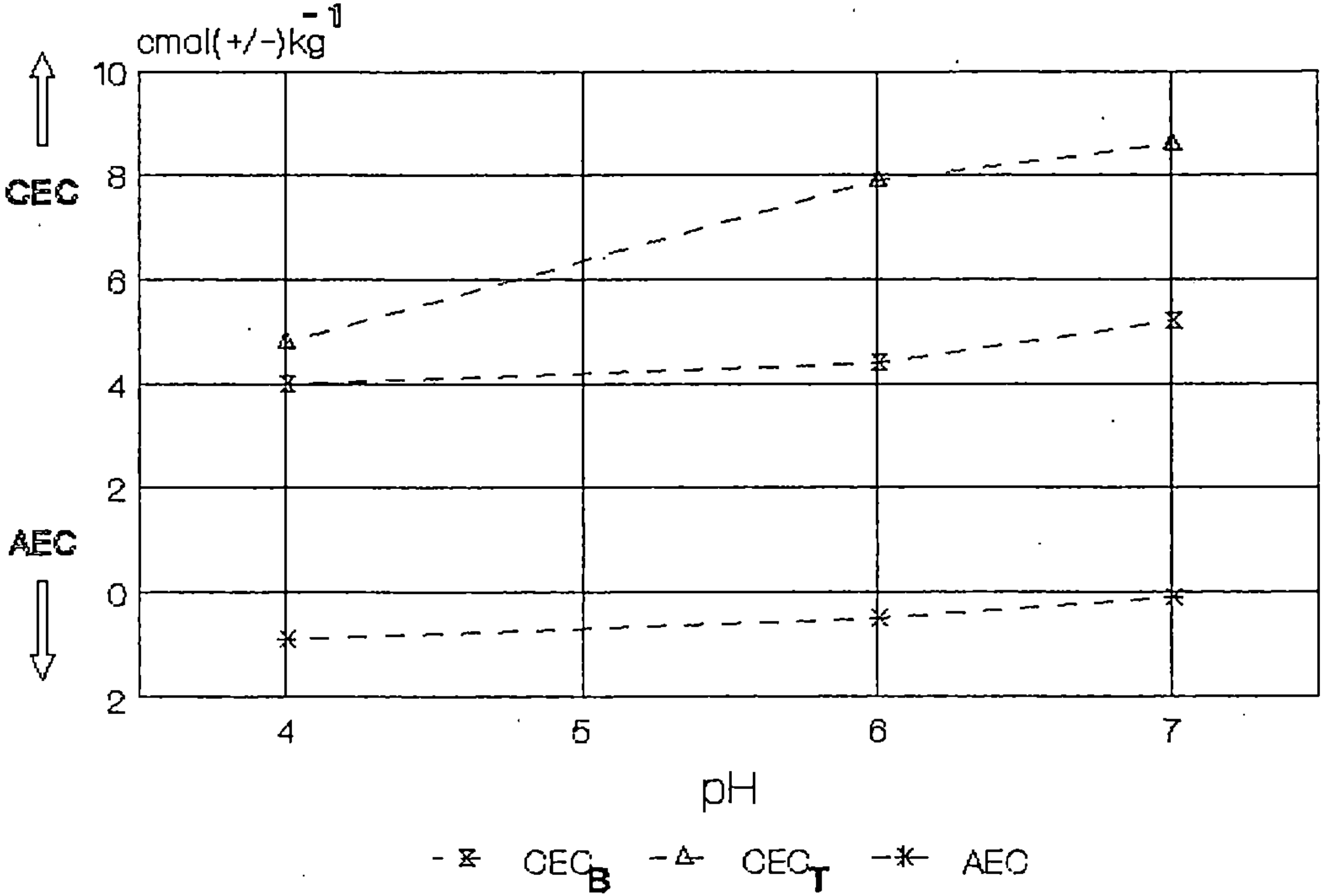


Fig. 37 : Curves of CEC_B CEC_T and AEC versus pH



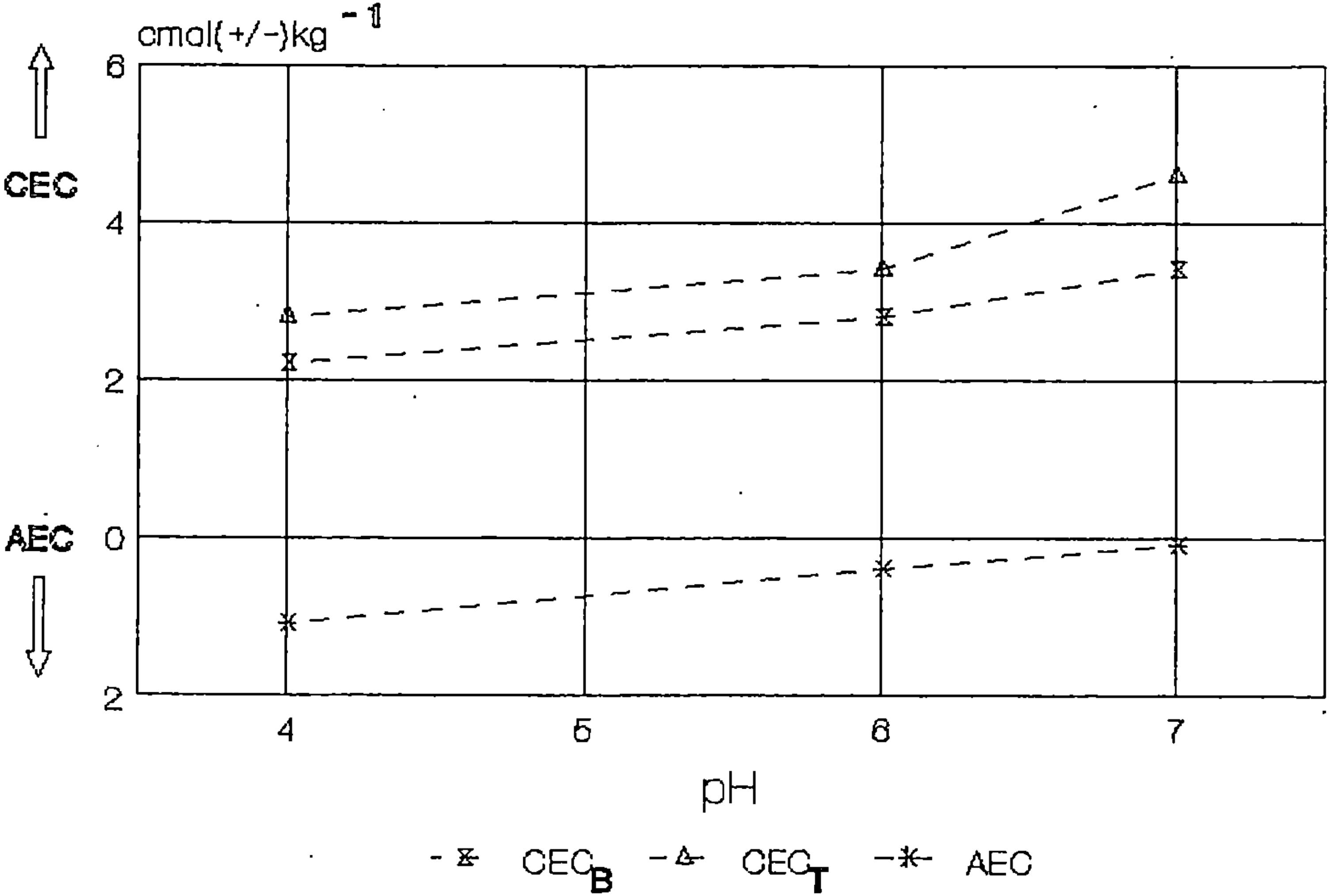
PLINTHUSTULT - Ap (Pilathara)

Fig. 38 : Curves of CEC_B, CEC_T and AEC versus pH



PALEUSTULT - A1 (Punalur)

Fig. 39 : Curves of CEC$_B$ CEC$_T$ and AEC versus pH



HAPLUSTOX - Ap (Pachalloor)

Table 11. Analysis of variance of the data obtained for CEC as determined by direct measurement of retention of ions

Source of variation	D.F.	M.S.S.	F
Electrolyte	3	2.79	60.50**
Soil	7	19.90	432.60**
pH	3	46.20	1004.50**
Electrolyte x soil	21	0.19	4.07**
Soil x pH	21	0.71	15.37**
Electrolyte x pH	9	0.24	5.12**
Electrolyte x soil x pH	63	0.047	1.00

** Significant at 1% level.

Table 12. Average effects of treatments

Electrolyte	Soil		pH
E_1 = 4.50	S_1 = 4.38	S_5 = 5.74	pH_3 = 2.68
E_2 = 3.93	S_2 = 2.68	S_6 = 2.87	pH_5 = 3.70
E_3 = 4.09	S_3 = 5.46	S_7 = 4.31	pH_6 = 4.40
E_4 = 3.83	S_4 = 3.87	S_8 = 3.40	pH_8 = 5.50

F	60.53	432.57	1004.49
CD	(0.05) 1.07	0.152	0.107

Table 13. AEC as influenced by different electrolytes in different soils at different pH.

Electrolytes.	Soils								pH			
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	pH_3	pH_5	pH_6	pH_8
E_1	0.83	1.75	1.03	0.90	0.68	1.65	1.45	1.88	2.15	1.68	0.90	0.35
E_2	0.53	1.28	0.75	0.60	0.50	1.43	1.33	0.85	1.75	1.19	0.54	0.15
E_3	0.70	1.50	0.90	0.83	0.68	1.33	1.35	1.45	1.93	1.53	0.64	0.28
E_4	0.58	1.25	0.70	0.68	0.63	1.18	1.34	1.28	1.73	1.23	0.63	0.23

pH								
pH_3	1.25	1.97	1.83	1.40	1.25	2.38	2.53	2.50
pH_5	0.73	1.83	1.00	1.10	0.73	2.03	2.00	1.83
pH_6	0.43	1.35	0.35	0.38	0.38	0.93	0.74	0.88
pH_8	0.23	0.63	0.20	0.13	0.13	0.25	0.20	0.25

F = (E) = 34.14
F = (S) = 86.67
F = (pH) = 687.6
F = (ExS) = 2.99
F = (SxpH) = 12.74
F = (ExpH) = 2.06

CD (0.05) E = 0.08
CD (0.05) S = 0.11
CD (0.05) pH = 0.08
CD (0.05) ExS = 0.22
CD (0.05) SxpH = 0.22
CD (0.05) ExpH = 0.16

Table 14. Analysis of variance of the data obtained for AEC as determined by direct measurement of retention of ions.

Source of variation	D.F.	M.S.S.	F
Electrolyte	3	0.85	34.15**
Soil	7	2.16	86.67**
pH	3	17.12	687.61**
Electrolyte x Soil	21	0.07	2.99**
Soil x pH	21	0.32	12.74**
Electrolyte x pH	9	0.05	2.06*
Electrolyte x Soil xpH	63	0.024	1.00

* Significant at 5 per cent level
** Significant at 1 per cent level

Table 15. Average effects of treatments.

Electrolyte	Soil		pH
E_1 = 1.27	S_1 = 0.66	S_5 = 0.62	pH_3 = 1.89
E_2 = 0.91	S_2 = 1.44	S_6 = 1.39	pH_5 = 1.40
E_3 = 1.09	S_3 = 0.84	S_7 = 1.37	pH_6 = 0.68
E_4 = 0.95	S_4 = 0.75	S_8 = 1.36	pH_8 = 0.25
F 34.15	86.67		687.61
CD 0.08 (0.05)	0.11		0.08

Table 16. Regression of CEC/AEC on pH

Electrolyte	Regression equation	F	R^2 %	r
0.20 N KCl	CEC = 0.9356 + 0.6481 pH	27.63**	47.95	0.69
	AEC = 3.34 - 0.38 pH	47.79**	61.43	0.78
0.05 N KCl	CEC = 1.0274 + 0.5274 pH	27.07**	47.44	0.69
	AEC = 2.74 - 0.33 pH	54.58**	64.52	0.80
0.10 N $CaCl_2$	CEC = 0.6875 + 0.6187 pH	25.76**	46.20	0.68
	AEC = 3.02 - 0.35 pH	53.96**	64.26	0.80
0.01 N $CaCl_2$	CEC = 1.0125 + 0.5124 pH	22.53**	22.89	0.65
	AEC = 2.66 - 0.311 pH	61.65**	67.26	0.82

** Significant at 1% level

Table 17 : Summary of results of CEC and AEC by various methods

Sample / Location	Horizon	CEC (cmol (p⁺) kg⁻¹)							AEC (cmol (e) kg⁻¹)				
		Ammo. Ace. pH_7 (M1)	ECEC (M2)	Comp. Exch. (M3)	0.2N KCl (M4)	0.2N NaCl (M5)	CEC_T (M6)	CEC_B (M7)	Comp. Exch. (M1)	0.2N KCl (M2)	0.2N NaCl (M3)	P-adsorption (M4)	0.002 M $CaCl_2$ (M5)
Kandiustult (Pilicode)	Ap	9.6	3.6	3.6	4.1	4.0	4.2	3.2	0.2	0.9	0.8	0.8	0.9
Kandiustult (Pilicode)	B_1	4.1	3.8	2.0	2.0	2.1	3.1	2.1	0.9	2.1	1.9	2.1	1.6
Plinthustult (Pilathara)	Ap	6.8	4.9	3.5	5.6	5.4	4.5	3.2	0.1	1.3	1.0	0.8	0.6
Plinthustult (Pilathara)	B_{21}	5.2	3.5	1.9	3.6	3.4	3.5	2.1	1.1	1.5	1.3	1.6	1.3
Paleustult (Punalur)	A_1	13.0	6.6	3.8	6.8	6.1	6.6	4.2	0.2	1.0	0.8	1.2	0.6
Paleustult (Punalur)	Bt_2	5.1	2.4	2.3	2.6	2.3	3.3	2.5	1.7	2.3	2.1	2.4	1.8
Kandiustult (Arackal)	Ap	5.9	2.6	2.9	4.1	4.1	3.6	2.9	0.3	1.0	0.9	1.0	0.5
Kandiustult (Arackal)	B_{22}	3.1	4.3	1.9	2.3	2.4	2.7	2.0	1.0	2.1	1.9	1.8	1.0
Haplustult (Karakulam)	Ap	5.9	4.9	3.4	4.0	3.8	4.5	3.4	0.3	0.9	0.7	0.4	0.8

(Contd.)

Table 17 : Summary of results of CEC and AEC by various methods (Contd.)

Sample / Location	Horizon	CEC (cmol (p$^+$) kg^{-1})							AEC (cmol (e) kg^{-1})				
		Ammo. Ace. pH$_7$ (M1)	ECEC (M2)	Comp. Exch. (M3)	0.2N KCl (M4)	0.2N NaCl (M5)	CEC$_T$ (M6)	CEC$_B$ (M7)	Comp. Exch. (M1)	0.2N KCl (M2)	0.2N NaCl (M3)	P-adsorption (M4)	0.002 M CaCl$_2$ (M5)
Haplustult (Karakulam)	B$_2$	6.6	6.4	3.4	4.1	3.9	4.1	2.2	0.5	1.2	1.0	1.1	1.2
Kandiustult (Maruthur)	Ap	6.7	4.9	4.0	3.9	3.9	4.2	4.1	0.2	0.6	0.4	0.8	0.5
Kandiustult (Maruthur)	B$_2$	4.3	4.1	2.3	2.6	2.8	2.4	2.0	0.9	2.2	2.1	1.6	0.7
Haplustox (Pachalloor)	Ap	8.7	2.9	2.2	4.3	4.1	3.1	2.3	1.2	2.1	2.0	2.4	0.9
Haplustox (Pachalloor)	BA	4.6	3.0	1.2	2.6	2.4	1.6	1.5	2.1	2.7	2.5	2.6	1.3

Table 18. Methods of CEC and AEC determinations - Comparison of mean values.

Methods	Mean values	
	CEC	AEC
M_1	6.40	0.76
M_2	4.14	1.56
M_3	2.74	1.39
M_4	3.76	1.47
M_5	3.62	0.98
M_6	3.67	
M_7	2.69	
F 10.52**		4.30*
CD (0.05)	1.07	0.47

** Significant at 1% level
* Significant at 5% level

Table 19. Permanent charge determined by different methods

Soil/Location	Horizon	Permanent charge from ion adsorption data cmol $(p^+/^-e)$ kg^{-1}						Measured cmol$(p^+/^-e)kg^{-1}$	Calculated cmol$(p^+/^-e)kg^{-1}$	From potentiometric titration curve cmol $(p^+/^-e)$ kg^{-1}
		0.2 N KCl	0.05 N KCl	0.1 N $CaCl_2$	0.01 N $CaCl_2$	CEC_T	CEC_B			
Kandiustult (Pilicode)	A_p	2.5	2.4	2.2	2.1	3.0	2.0	1.9	0.8	2.0
Plinthustult (Pilathara)	A_p	2.8	2.5	2.6	2.9	2.5	1.5	2.1	1.4	2.4
Paleustult (Punalur)	A_1	3.3	2.9	2.9	3.1	3.5	2.8	2.6	2.6	2.4
Haplustox (Pachalloor)	A_p	1.1	1.4	1.4	1.2	1.8	1.3	1.1	1.7	2.2

Gillman and Uehara (1980) was 1.9 cmol (q) kg^{-1} in the Kandiustult-Ap of Pilicode, 2.1 in the Plinthustult- Ap of Pilathara, 2.6 in the Paleustult-A1 of Punalur and 1.1 in the Haplustox-Ap of Pachalloor. Permanent negative charges calculated from the curves of ion,adsorption experiments were also in agreement with the above data. Theoretically calculated values and values obtained from the potentiometric tiration curves showed similar results.

6. Contribution of organic matter and sesquioxides to exchange properties of soils.

The results are presented in Table 20 and 21. All the samples after removal of organic matter by peroxide treatment showed a decrease in CEC but the AEC in every instance slightly increased after peroxidation. There was no exception to this trend though the change in CEC and AEC consequent to peroxide treatment varied considerably among samples.

Regression of CEC and AEC on organic carbon indicated that nearly 64.34 per cent of CEC and 8 per cent of AEC was contributed by the organic matter. The effect of removal of organic matter on AEC indicated was negative though not significant statistically. Removal of R_2O_3 accounted for nearly 11 per cent of the change in CEC and 22 per cent of the change in AEC, both non-significant statistically. However the combined effect of organic matter and R_2O_3 on both CEC and AEC was highly significnt as evidenced from the multiple linear regression equation. Almost 59 and 50 per cent of the CEC and AEC respectively was contributed by the combined effect of organic matter and R_2O_3.

7. Mineralogical analysis of clay fraction

7.1 X-ray diffraction analysis (XRDA)

X-ray diffractograms of soil clay fractions of the various profiles studied are presented in figures 40 to 46. The XRDA data and the interpretation in terms of the dominant minerals present are given in Tables 22(a) and 22(b). The major minerals identified are kaolinte, vermiculite, chlorite, gibbsite, quartz and goethite. There was considerable shifting of the baseline of the diffractograms indicating the presence of amorphous minerals. This was particulrly noticed in the Plinthustult- B_1 of Pilathara, in the Kandiustult-B_2 of Pilicode, the Paleustult-Bt_2 of Punalur and in the Haplustult-B_2 of Karakulam. Appreciable amounts of smectite group minerals were present in all the samples except the Kandiustult-B_2 of Arackal and the Kandiustult-B_2 of Maruthur. The dominant clay mineral present in all the samples was kaolinite. Glycol solvation and heating did not give much additional information. However the presence of 2:1 type of minerals have been confirmed in many samples.

Table 20 Ion exchange capacity of selected samples as influenced by organic carbon and R_2O_3 content

Sample/ Location	Horizon	Organic Carbon %	R_2O_3 %	ION EXCHANGE CAPACITY $(cmol(P^+/e^-)kg^{-1}$							
				Untreated samples		After peroxide treatment		After DCB treatment		After peroxide and DCB treatment	
				CEC	AEC	CEC	AEC	CEC	AEC	CEC	AEC
Kandiustult (Pilicode)	A_p	1.96	41.0	3.6	0.2	1.4	0.3	4.8	0.2	2.6	0.0
"	B_1	1.02	25.0	2.0	0.9	1.4	1.0	4.1	0.2	2.1	0.1
Plinthustult (Pilathara)	A_p	1.51	22.1	3.5	0.1	1.2	0.3	4.2	0.0	1.9	0.0
"	B_{21}	0.67	32.5	1.9	1.1	1.3	1.4	2.3	0.2	2.0	0.3
Paleustult (punalur)	A_1	3.21	24.0	3.8	0.2	1.2	0.5	4.3	0.2	2.0	0.0
"	Bt_2	0.37	39.5	2.3	1.7	1.7	1.8	2.8	0.5	2.1	0.3

(Contd.)

Table 20 Ion exchange capacity of selected samples as influenced by organic carbon and R_2O_3 content (Contd.)

Sample/ Location	Horizon	Organic Carbon %	R_2O_3%	ION EXCHANGE CAPACITY (cmol(P^+/e^-)kg^{-1}							
				Untreated samples		After peroxide treatment		After DCB treatment		After peroxide and DCB treatment	
				CEC	AEC	CEC	AEC	CEC	AEC	CEC	AEC
Kandiustult (Arackal)	A_p	1.11	23.6	2.9	0.3	1.1	0.5	3.3	0.0	1.6	0.0
"	B_{22}	0.74	37.6	1.9	1.0	1.4	1.4	3.1	0.4	1.8	0.4
Haplustult (Karakulam)	A_p	1.32	23.7	3.4	0.3	1.0	0.3	4.8	-0.1	1.4	0.0
"	B_2	0.48	27.6	3.4	0.5	2.3	0.5	4.3	0.1	1.7	0.1
Kandiustult (Maruthur)	A_p	1.21	24.1	4.0	0.2	1.8	0.4	4.8	-0.3	2.5	0.0
"	B_2	0.27	31.2	2.3	0.9	1.6	0.9	2.5	0.1	1.7	0.3
Haplustox (Pachalloor)	A_p	0.87	36.6	2.2	1.2	0.9	1.5	3.1	0.1	1.2	0.4
"	BA	0.24	34.0	1.2	2.1	0.8	1.4	1.8	0.1	1.2	0.3

Table 21. Simple and multiple linear regressions relating CEC, AEC
O.C and R_2O_3 of selected samples.

	F	R^2%	r
Regression of CEC and AEC on Organic Carbon.			
1. CEC = 0.4698 + 0.8540.0.C	21.65**	64.34	0.80
2. AEC = 0.0029 + 0.09.0.C	1.05(ns)	8.00	0.28
Regression of CEC and AEC on R_2O_3			
3. CEC = 0.072 + 0.025 R_2O_3	1.49(ns)	11.00	0.33
4. AEC = 0.5469 + 0.0377 R_2O_3	3.39(ns)	22.00	0.47
Multiple linear regression of CEC and AEC on organic carbon and R_2O_3			
5. CEC = 2.3412 + 0.3662 OC − 0.0559 R_2O_3	7.98**	59.20	0.77
6. AEC = 0.0099 − 0.2833 OC + 0.0288 R_2O_3	5.43**	49.67	0.70

** Significant at 1 % level
ns. not significant

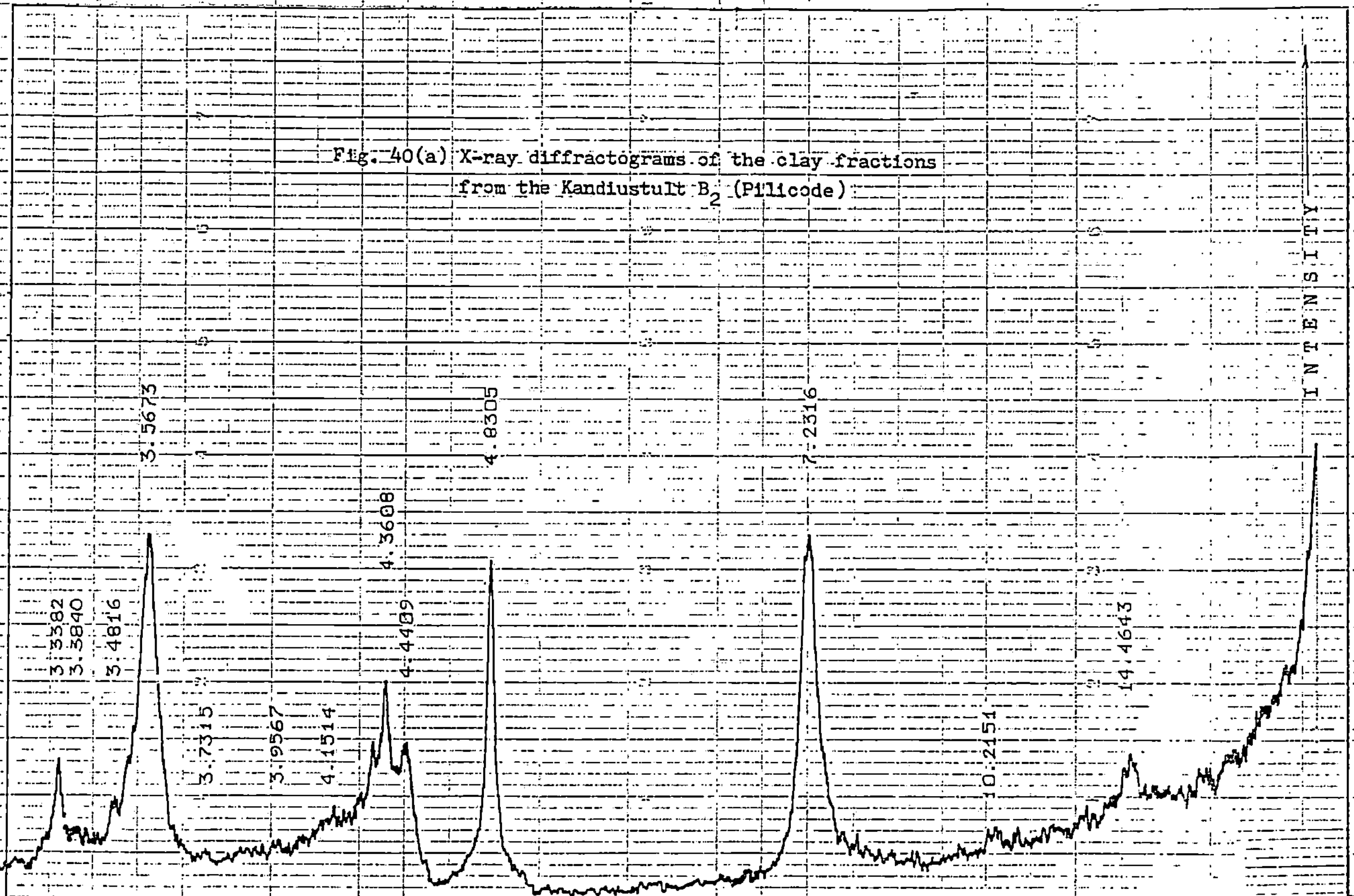


Fig. 40(a) X-ray diffractograms of the clay fractions from the Kandiustult B_2 (Pilicode)

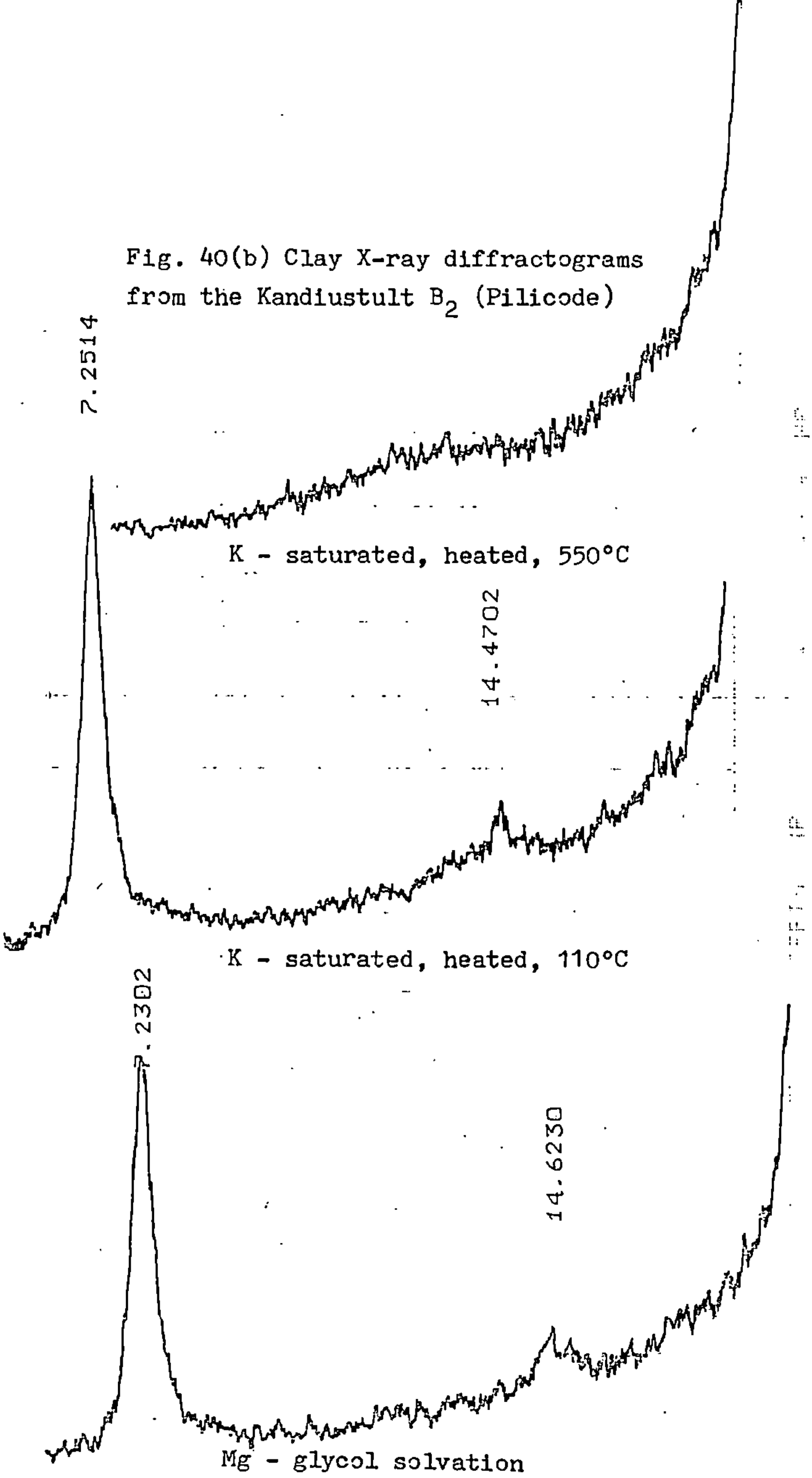
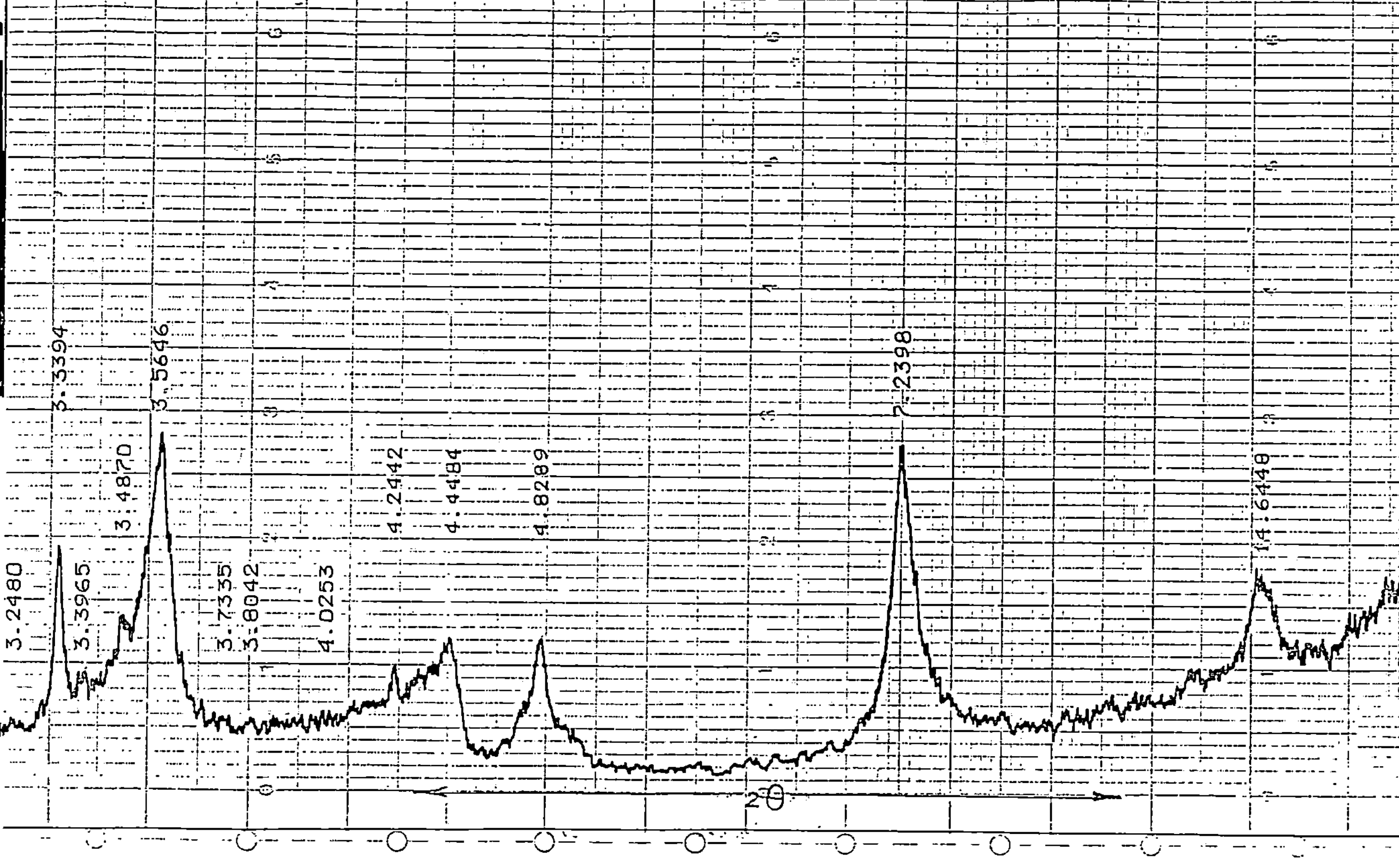


Fig. 40(b) Clay X-ray diffractograms from the Kandiustult B_2 (Pilicode)

Fig. 41(a) X-ray diffractograms of the clay fractions from the Plinthustult B_1 (Pilathara)



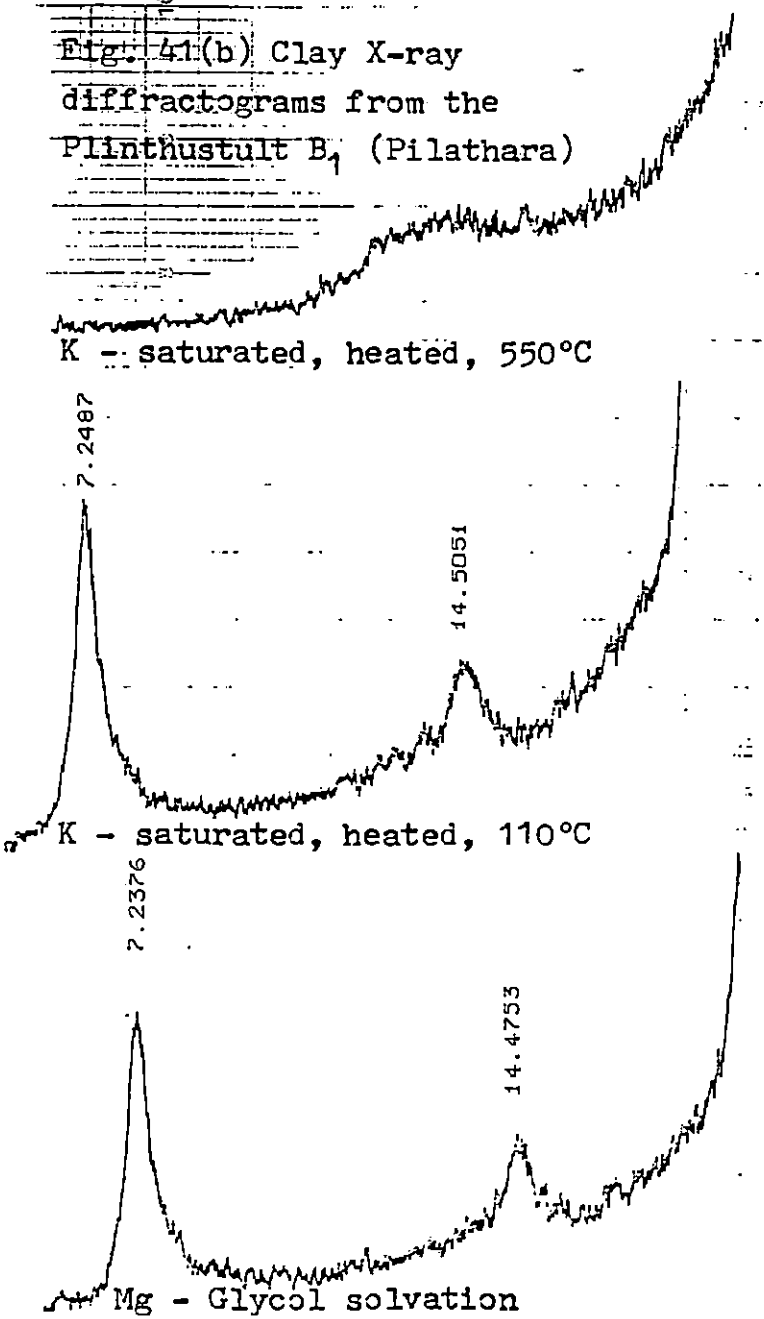


Fig. 41(b) Clay X-ray diffractograms from the Plinthustult B_1 (Pilathara)

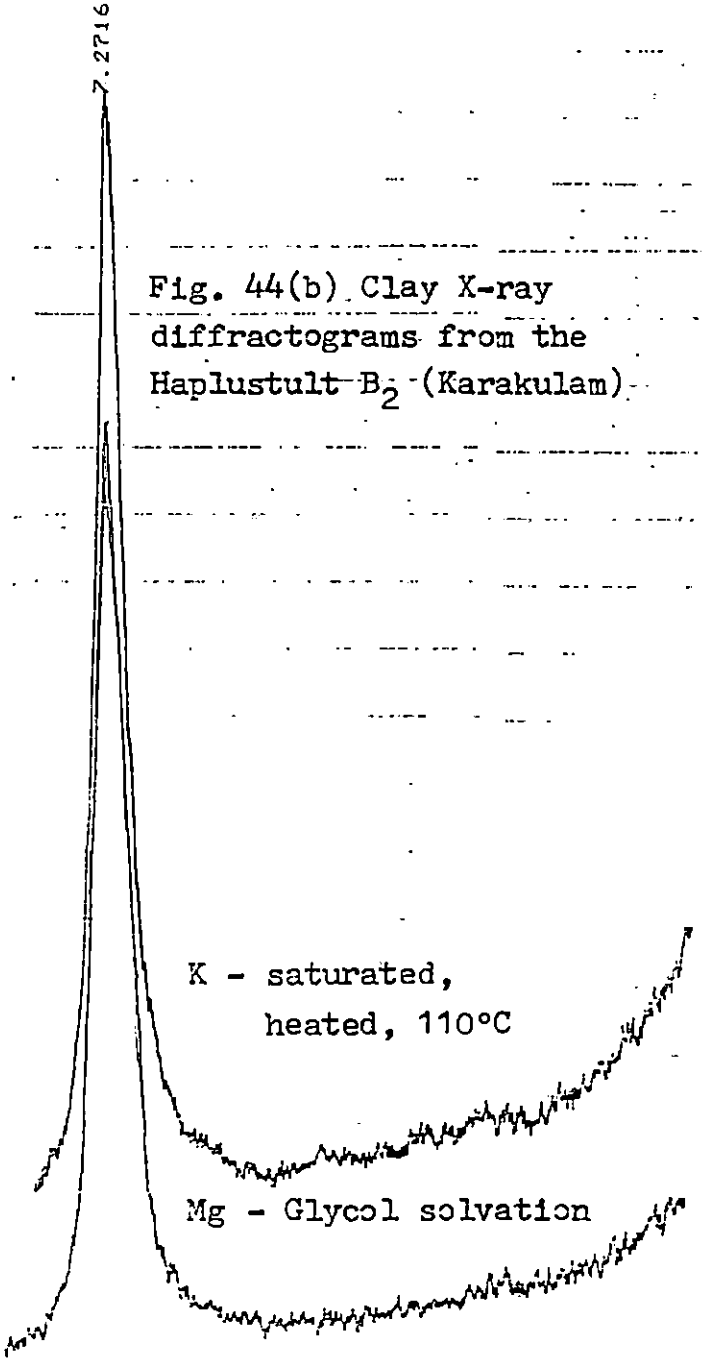


Fig. 44(b) Clay X-ray diffractograms from the Haplustult B_2 (Karakulam)

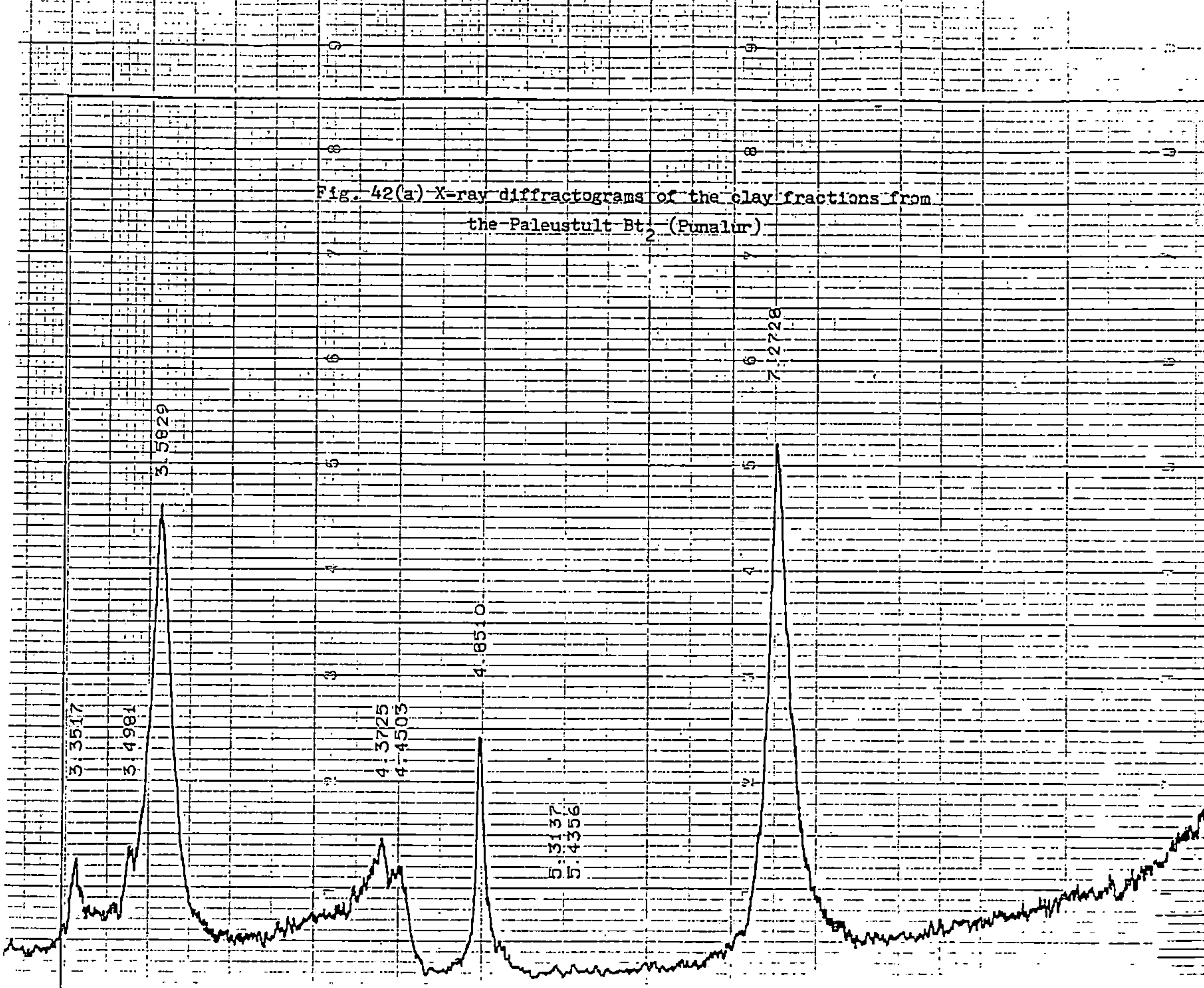


Fig. 42(a) X-ray diffractograms of the clay fractions from the Paleustult Bt_2 (Punalur)

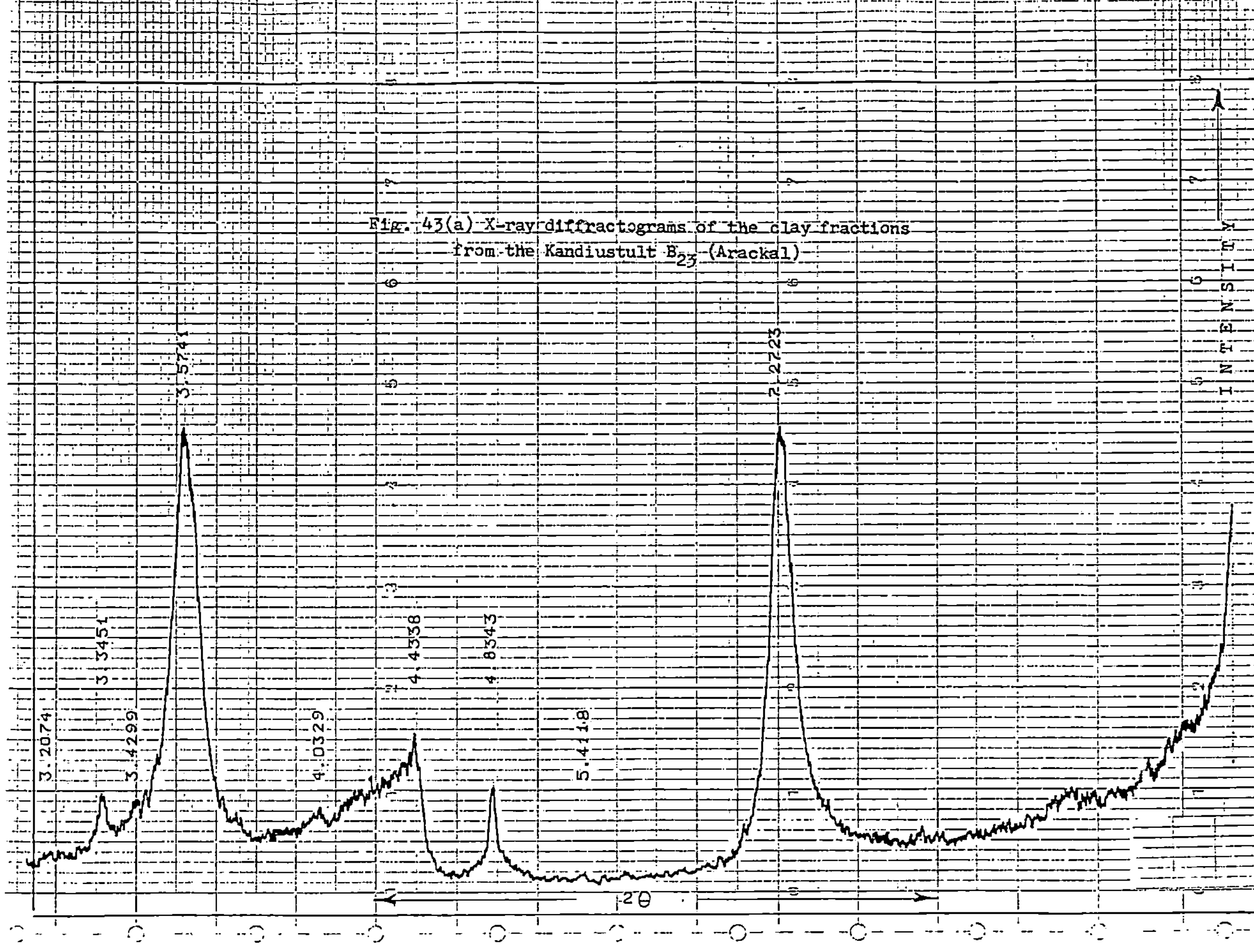


Fig. 43(a) X-ray diffractograms of the clay fractions from the Kandiustult B_{23} (Arackal)

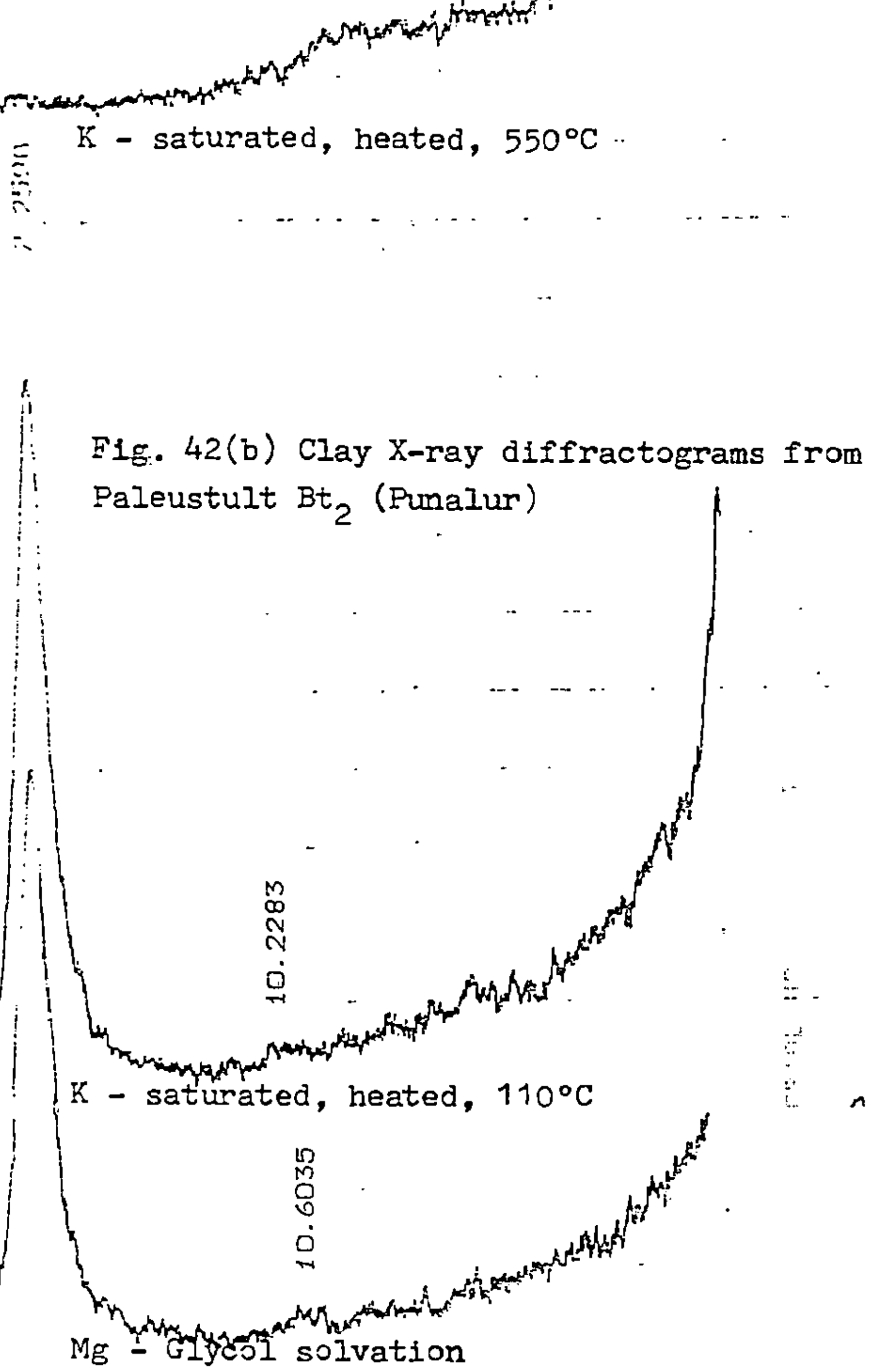


Fig. 42(b) Clay X-ray diffractograms from the Paleustult Bt_2 (Punalur)

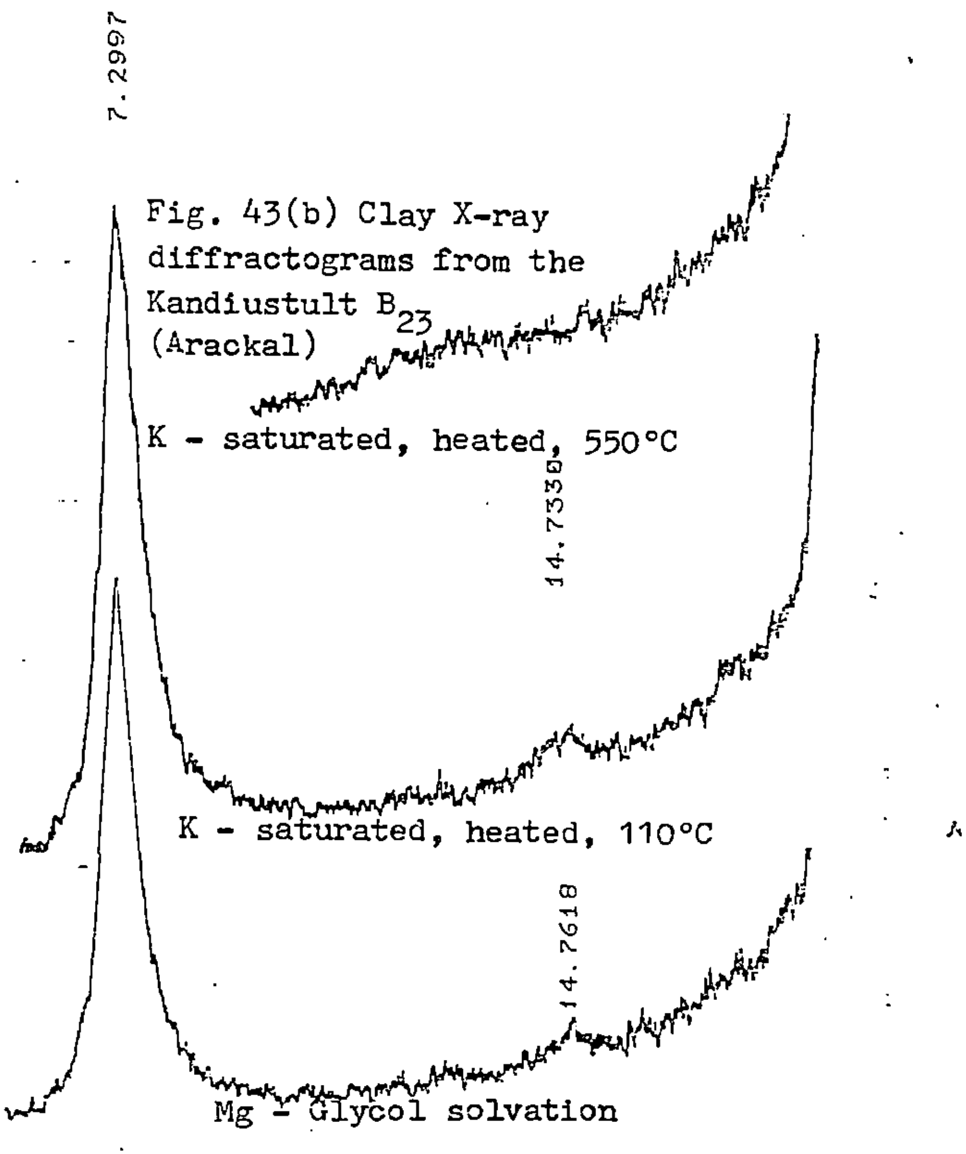


Fig. 43(b) Clay X-ray diffractograms from the Kandiustult B_{23} (Arackal)

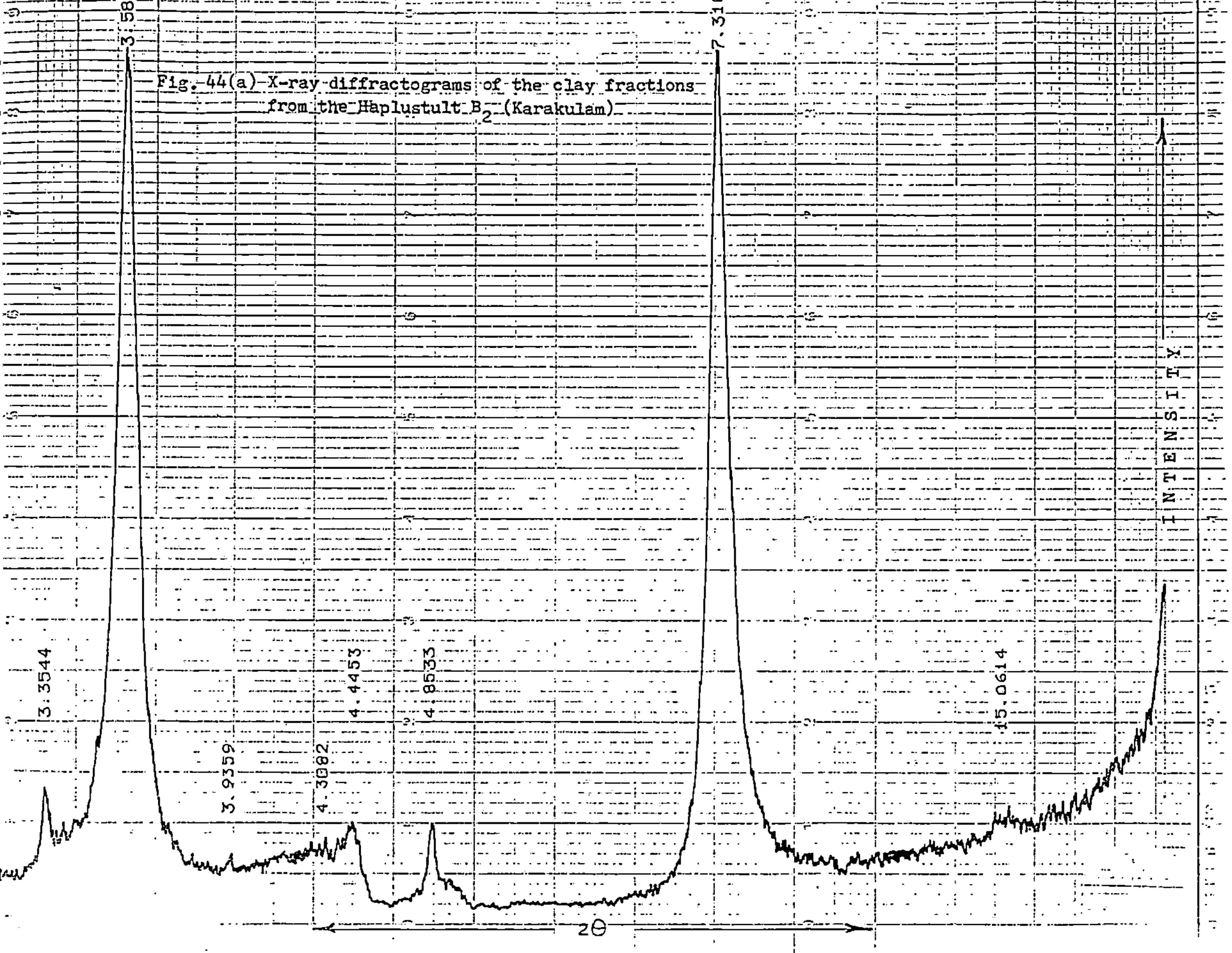


Fig. 44(a) X-ray diffractograms of the clay fractions from the Haplustult B_2 (Karakulam)

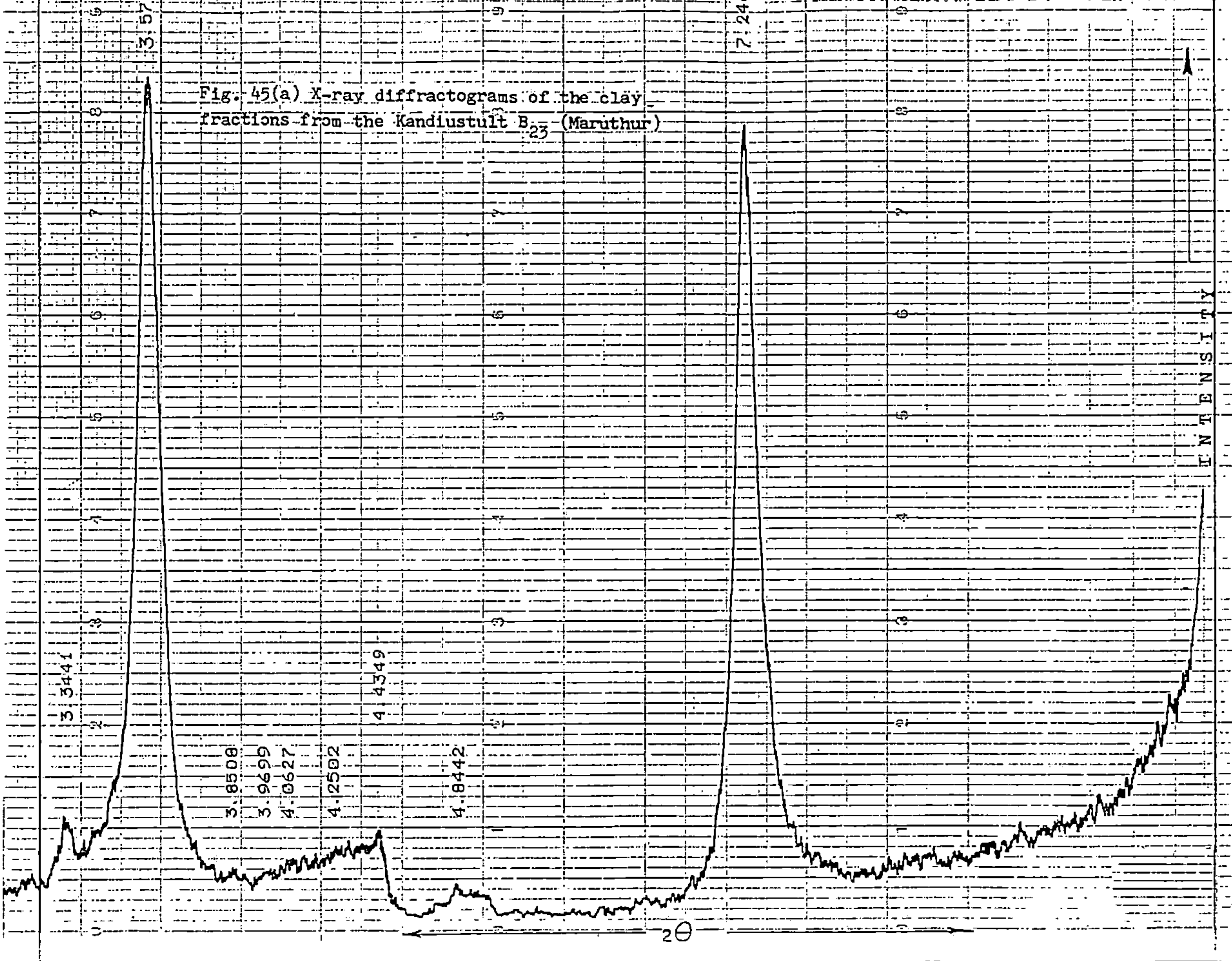


Fig. 45(a) X-ray diffractograms of the clay fractions from the Kandiustult B_{23} (Maruthur)

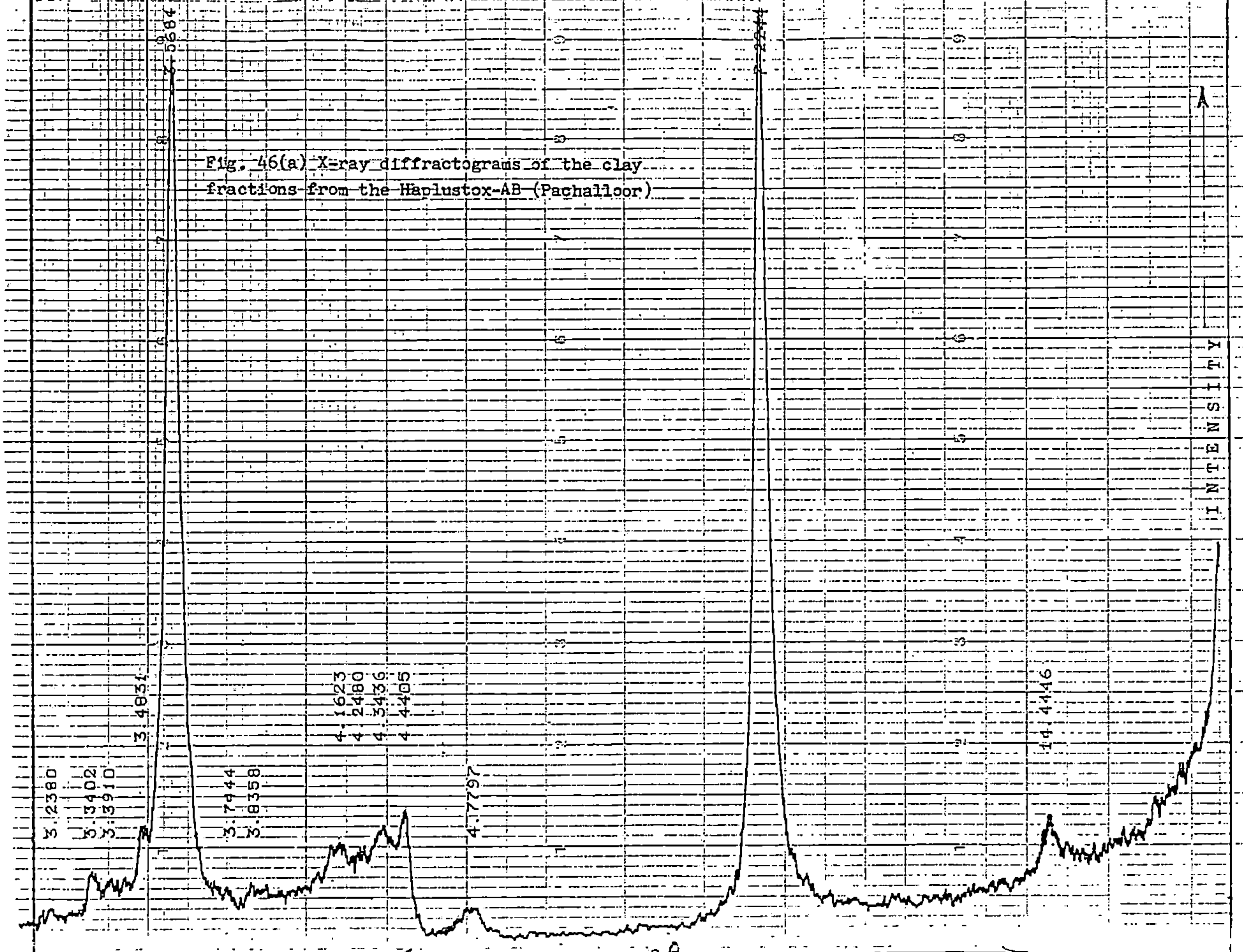


Fig. 46(a) X-ray diffractograms of the clay fractions from the Haplustox-AB (Pachalloor)

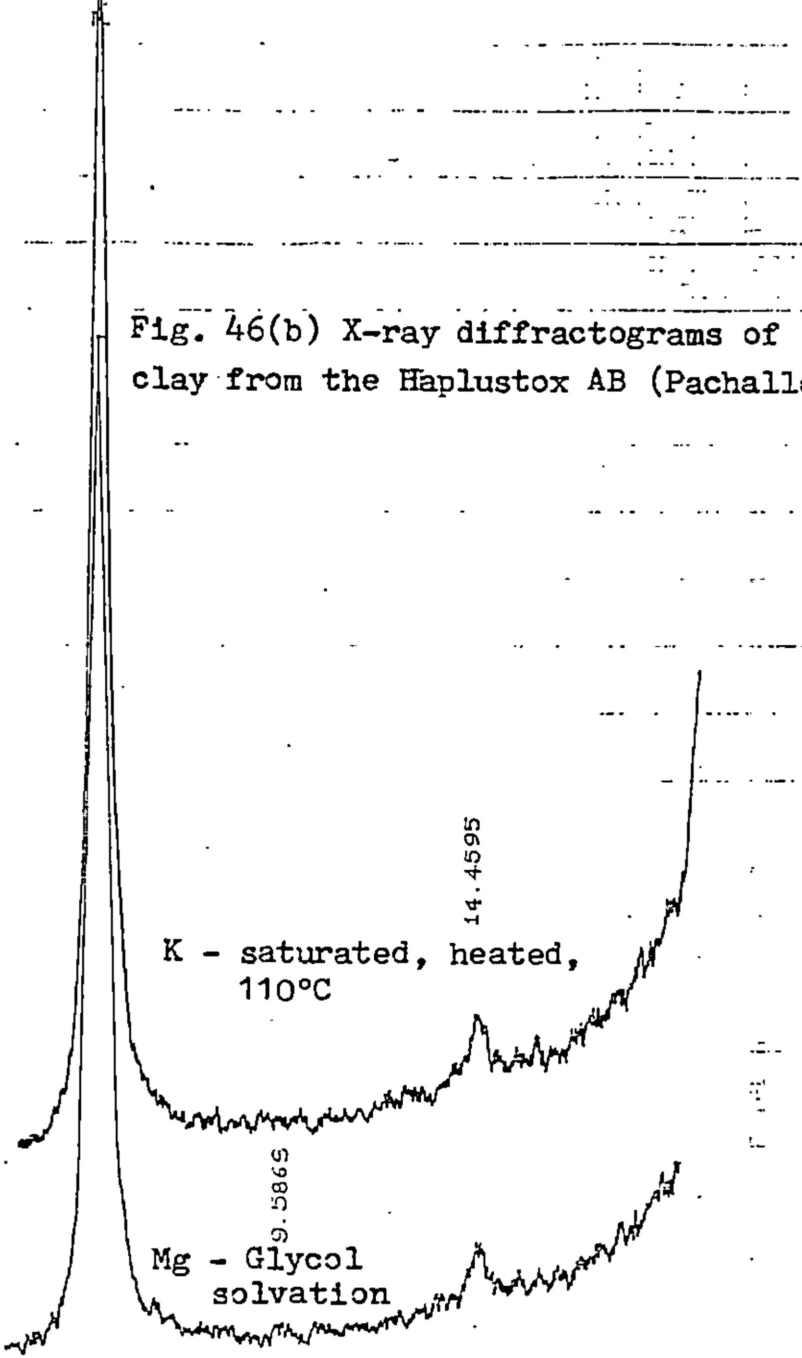


Fig. 46(b) X-ray diffractograms of clay from the Haplustox AB (Pachalloor)

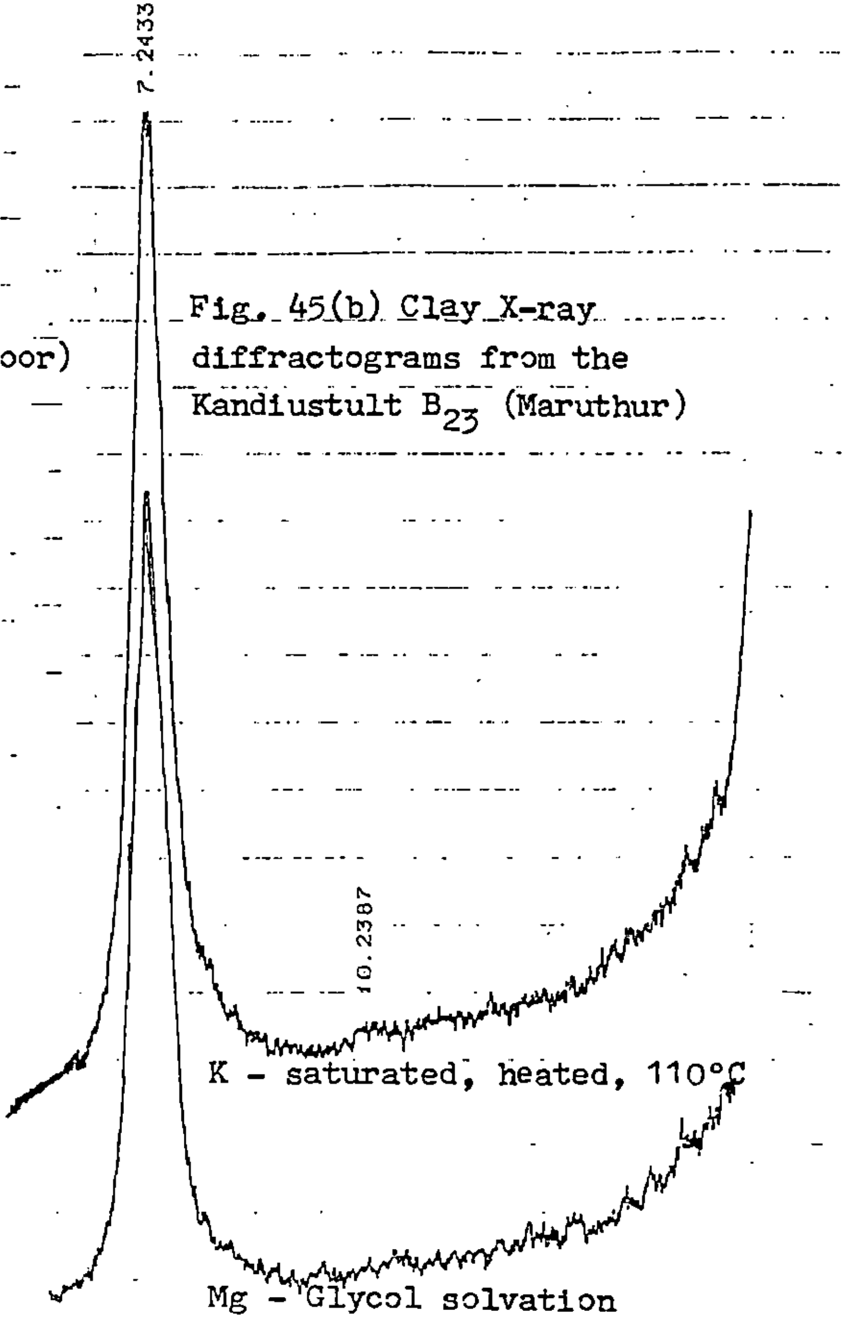


Fig. 45(b) Clay X-ray diffractograms from the Kandiustult B_{23} (Maruthur)

Table 22 (a). XRD-data of fine clay fraction (After DCB- treatment)

Sl. No	Sample-Location	Horizon	d-spacing A°	Relative intensity	Mineral/s identified
1.	Kandiustult (Pilicode)	B_2	14.4643	1.4	Vermiculite
			10.2151	< 1.0	Halloysite/Illite
			7.2316	3.3	Kaolinite
			4.8305	3.1	Chlorite, Gibbsite
			4.4409	1.5	Illite,Muscovite
			4.3608	2.0	Kaolinite
			4.1514	< 1.0	Dickite
			3.9567	<1.0	Kaolinite
			3.7315	<1.0	Feldspars
			3.5673	3.3	Kaolinite
			3.4816	1.0	Feldspars
			3.3840	<1.0	Goethite
			3.3382	1.3	Gibbsite, Quartz
2.	Plinthustult (Pilathara)	B_1	14.6448	1.8	Vermiculite
			7.2398	2.8	Kaolinite
			4.8289	1.2	Gibbsite, chlorite
			4.4484	1.2	Nacrite
			4.2442	1.0	Quartz
			4.0253	<1.0	Goethite
			3.8042	<1.0	Feldspars
			3.7335	<1.0	"
			3.5646	2.8	Kaolinite
			3.4870	1.4	Feldspars
			3.3965	<1.0	Goethite
			3.3394	1.9	Quartz
			3.2480	<1.0	Lepidocrocite

Table (contd.....)

3.	Paleustult (Punalur)	Bt_2	14.2718	3.5	Vermiculite, chlorite
			12.6340	2.8	Vermiculite
			7.2728	5.2	Kaolinite
			4.8510	2.4	Chlorite, Gibbsite
			4.4503	1.2	Nacrite
			4.3725	1.5	Kaolinite
			3.5829	4.6	Kaolinite
			3.4981	1.4	Feldspars
			3.3517	1.3	Quartz
4.	Kandiustult (Arackal)	B_{23}	14.2710	1.2	Vermiculite Chlorite
			7.2723	4.6	Kaolinite
			4.8343	1.0	Chlorite, Gibbsite
			4.4338	1.6	Illite, Muscovite
			4.0329	<1.0	Goethite
			3.5741	4.5	Kaolinite
			3.4299	<1.0	Feldspars
			3.3451	1.0	Quartz
			3.2074	<1.0	Lepidocrocite
5.	Haplustult (Karakulam)	B_2	15.0614	1.2	Vermiculite Montmorillonite
			7.3102	8.6	Kaolinite
			4.8533	1.0	Gibbsite,chlorite
			4.4453	1.0	Nacrite
			4.3082	<1.0	Kaolinite
			3.9359	<1.0	"
			3.5853	8.6	"
			3.3544	1.3	Goethite

Table (contd....)

6.	Kandiustult (Maruthur	B_{23}	7.2469	7.9	Kaolinite
			4.8442	<1.0	Gibbsite, chlorite
			4.4349	1.0	Nacrite
			4.2502	<1.0	Gibbsite
			3.8508	<1.0	Kalolinite
			3.5712	8.3	"
			3.3441	1.1	"
7.	Haplustox (Pachalloor)	AB	14.4446	1.3	Vermiculite, chlorite
			7.2244	9.3	Kaolinite
			4.7797	<1.0	Gibbsite, cholrite
			4.4405	1.4	Nacrite
			4.3436	1.2	Kaolinite
			4.2480	1.0	Gibbsite
			4.1623	1.0	"
			3.8358	<1.0	Kaolinite
			3.7444	<1.0	Feldspars
			3.5684	8.8	Kaolinite
			3.4831	1.2	Feldspars
			3.3910	<1.0	Goethite
			3.3402	<1.0	Quartz

Table 22 (b). Summary of the mineral X-ray analyses of the fine clay fraction

Sl No	Sample/ Location	Horizon	Kaolinite	Chlorite, Vermiculite	Quartz	Gibbsite
1.	Kandiustult (Pilicode)	B_2	+	tr.-+	tr.	tr.-X
2.	Plinthustult (Pilathara)	B_1	+	+	tr.	tr.-X
3.	Paleustult (Punalur)	Bt_2	+-++	+	tr.	X
4.	Kandiustult (Arackal)	B_{23}	+-++	tr.	tr.	tr.-X
5.	Haplustult (Karakulam)	B_2	++	tr.	tr.	tr.-X
6.	Kandiustult (Maruthur)	B_{23}	++	-	tr.	o-tr.
7.	Haplustox (Pachalloor)	AB	++	tr.	tr.	tr.-X

tr. = Trace

+++ = Estimate of relative abundance

XXX = Non-clay minerals

7.2 Scanning election microscopic analysis.

The SEM pictures of the clay samples from the different profiles are presented in Plates 8 to 13. A thick coating of iron oxide was found in all the plates. Thick iron encrustations with amorphous materials were also seen in all the samples. The crystalline features were not visible even at very high magnifications (not photographed) during scanning due to the thick oxide coatings. Clay samples from the Paleustult-Bt2 showed appreciable amounts of organic matter as coating over the fabric.

No additional information could be obtained from the SEM pictures other than the occurrence of Fe, Al oxide coatings, organic matter coatings and amorphous materials.

8. Surface area estimation.

Data on specific surface determination of the selected samples are presented in Table 23. Measured values of all the samples were generally higher than the calculated values. Measured values by EGME impregnation method varied from 49-137 m^2g^{-1} whereas calculated values ranged from 32.91-108.64 m^2g^{-1}. The lowest measured value was given by the sub-surface horizon of the Haplustox from Pachalloor and the highest value for the Paleustult-Ap of Punalur. Calculated values closely followed the fluctuations in the negative co-ion adsorption. In the case of measured values, the contribution of organic matter towards specific surface was obvious as the values recorded was generally high for all the surface samples except the Kandiustult-Ap of Arackal.

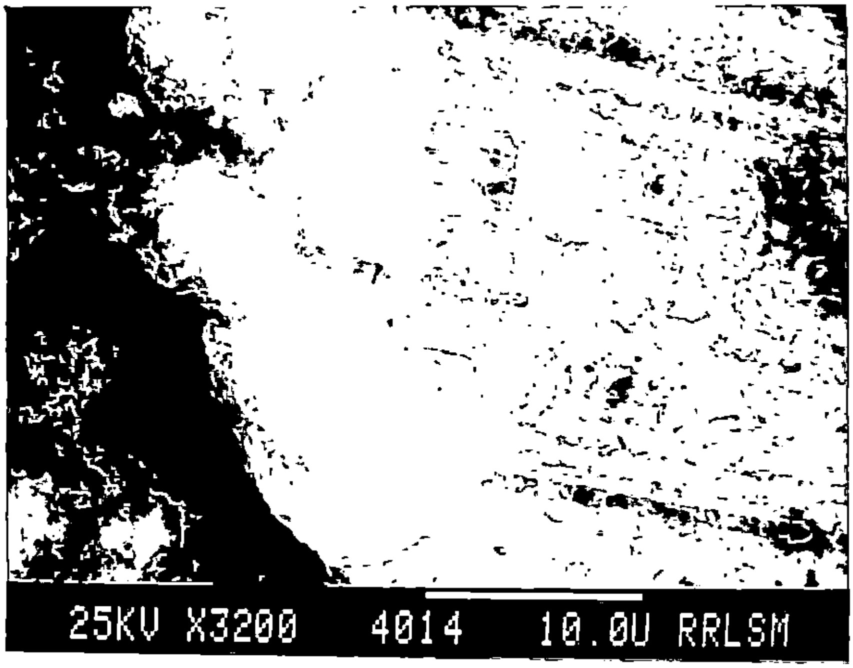


Plate: VIII Scanning electron photo micrograph of the fine clay from the Kandiustult B_2 - Pilicode.

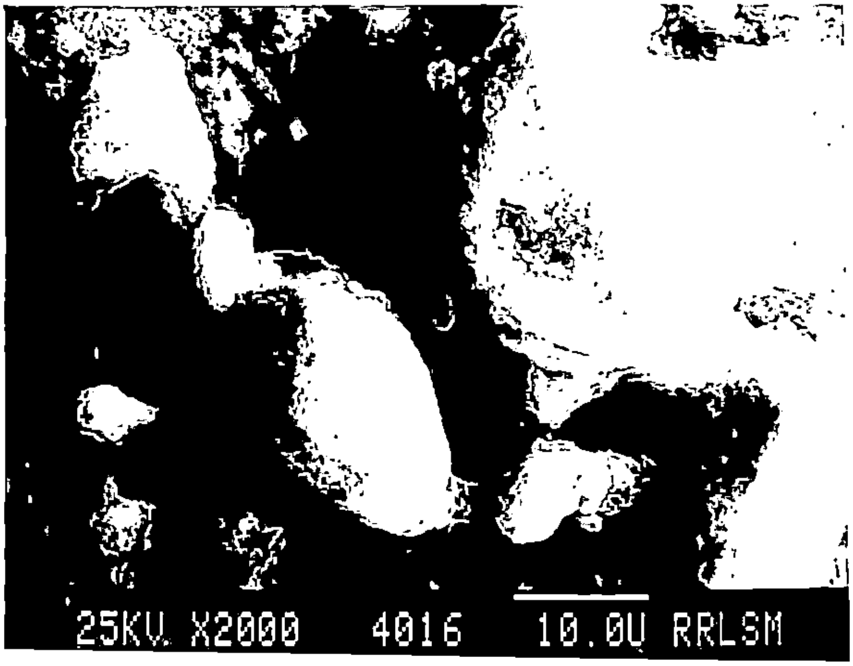


Plate: IX Scanning electron photo micrograph of the fine clay from the Plinthustult B_1 - Pilathara.

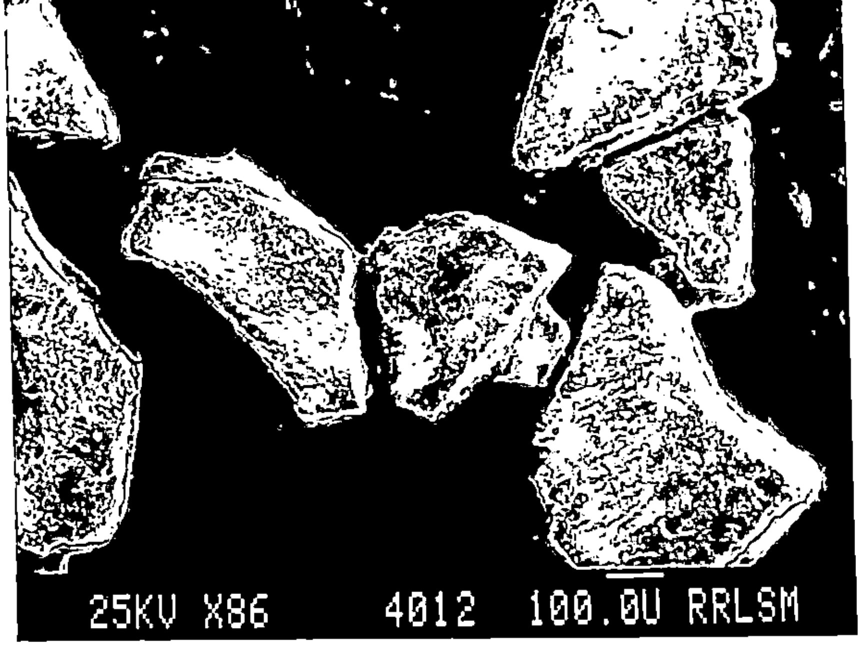


Plate: X Scanning electron photo micrograph of the fine clay from the Paleustult Bt_2 - Punalur.

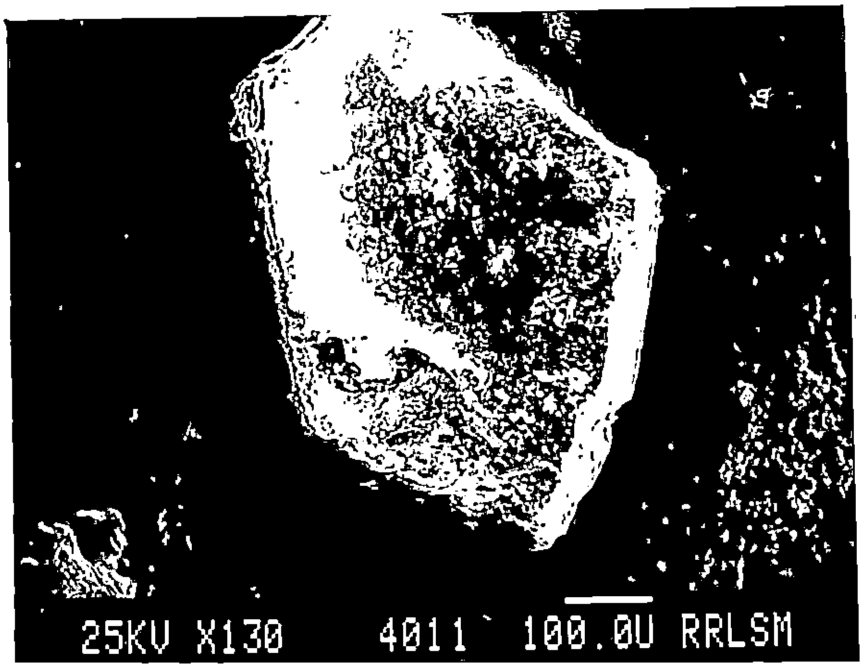


Plate: XI Scanning electron photo micrograph of the fine clay from the Haplustult B_2 - Karakulam.

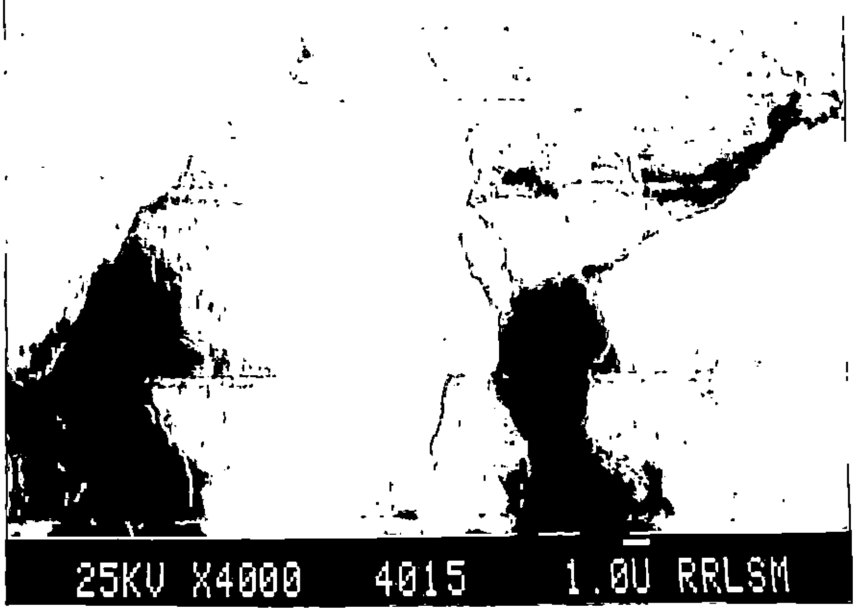


Plate: XII Scanning electron photo micrograph of the fine clay from the Kandiustult B_2 - Maruthur.

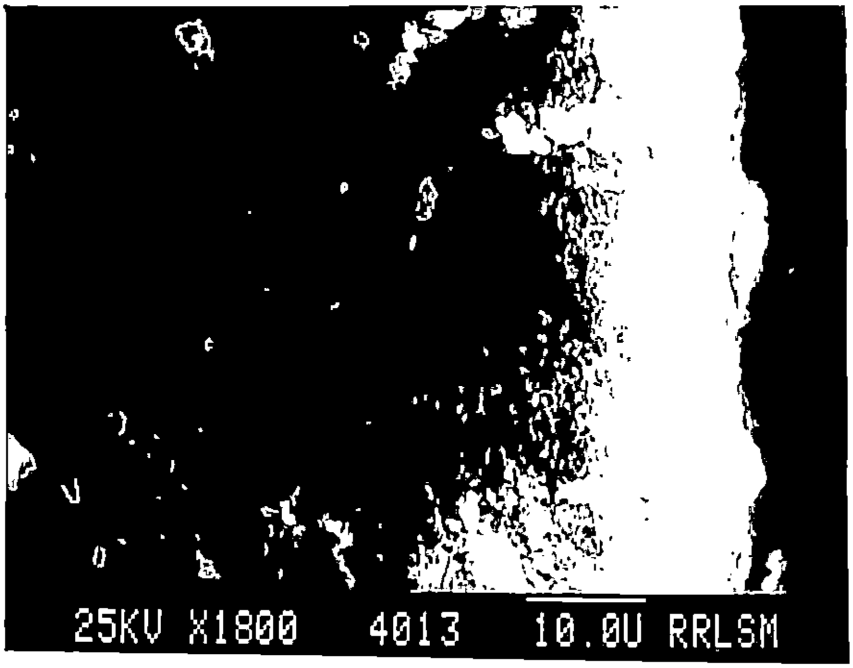


Plate: XIII Scanning electron photo micrograph of the fine clay from the Haplustox AB - Pachalloor.

Table 23. Specific surface of selected samples calculated from negative adsorption data and measured by ethylene glycol adsorption

Sample		Negative adsorption r^-	Total negative charge r	Specific surface m^2g^{-1} Calculated	Specific surface m^2g^{-1} Measured (EGME)
		cmol $(P^+/e^-)Kg^{-1}$			
Kandistult- (Pilicode)	A_p	0.20	4.4	34.46	90
"	B_1	0.19	3.8	32.91	81
"	B_2	0.24	3.7	42.34	68
plinthustult- (Pilathara)	A_p	0.34	5.8	59.50	98
"	B_1	0.26	4.8	45.26	77
"	B_{21}	0.31	5.8	53.92	79
Paleustult (Punalur)	A_1	0.60	7.1	108.64	137
"	A_2	0.30	4.6	52.95	108
"	$2Bt_2$	0.19	2.3	34.31	67
Kandiustult- (Arackal)	A_p	0.36	5.3	63.76	69
"	B_1	0.30	3.8	53.91	73
"	B_{22}	0.21	3.1	37.18	71
Haplustult - (Karakulam	A_p	0.31	4.8	54.67	87
"	B_1	0.28	5.3	48.66	64
"	B_2	0.43	5.8	76.78	57
Kandiustult- (Maruthur)	A_p	0.36	4.4	64.95	84
"	B_1	0.41	3.8	76.82	69
"	B_2	0.19	3.1	33.37	54
Haplustox- (Pachalloor)	A_p	0.40	5.3	71.55	91
"	AB	0.38	4.8	68.30	61
"	BA	0.22	3.6	38.63	49

DISCUSSION

DISCUSSION

1. Charge Contributing factors and their inter-relationships.

There has been considerable interest in soil fertility studies of the highly weathered soils of Kerala in recent years, particularly in view of the low crop yields often encountered. One of the major electro-chemical properties of the soils instrumental for the poor fertility, namely the ion exchange capacity or the charge character was not given much attention, rather was ignored till recently. It is now realised that a better understanding of the forces which operate near the particle surfaces to cause the retention of ions is needed, in order to institute management procedures which will allow maximum production from these soils.

One of the major features of many highly weathered soils in the tropics is the predominance of Kaolinite and hydrous oxides of iron and aluminium 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 sign of surface charge of oxide minerals depends on a variety of factors such as p^H, nature and concentration of electrolytes present in the soil solution, their interaction with organic matter, nature and quantity of amorphous materials and their ratio with crystalline minerals in the clay fraction (Wild,1988).

Although the soil is a complex system, from the 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 highly weathered upland soils of the tropics, the constant potential colloids such as iron and aluminium oxides, certainly play a dominant role in influencing the physico- chemical properties.

In a soil colloidal system several parameters contribute towards charge development and the variations in their ion-exchange capacity have to be attributed to variations and different combinations of contributing factors in the soil. Indepth studies of a similar nature have not been hitherto attempted in the low activity clay soils of India.

The studies conducted have to be classified as effects of various charge contributing factors on parameters of measurement to enable assessment of both the contribution of the factors in different soils as well as the suitability of the parameters themselves for such measurements.

The important parameters of charge assessment, the charge contributing factors and their inter-relationships are presented in tables 2 to 4. The path coefficient analysis showing the direct and indirect effects of charge contributing factors to the major parameters of the measurement of charge namely CEC and AEC presented in tables 5 to 8 is discussed below.

1.1 Effect of Charge contributing factors on cation exchange capacity

The maximum positive correlation was obtained with organic carbon (0.843) and maximum negative correlation (- 0.440)was observed with clay content. Fe_o and Al_o(0.471;0.473) also recorded significant positive correlations with cation exchange capacity. The effect of organic carbon on CEC is direct and as expected, contributed from the ionization of various functional groups like amines, carbonyl, carboxyl, enolic hydroxyl, phenolic hydroxyl, quinonic hydroxyl, and heterocyclic nitrogen compounds through the protonation-deprotonation mechanisms (Raman, 1986). The highly significant negative correlation with clay content obviously indicate the presence of appreciable amounts of Fe, Al hydrous oxides having very low CEC in the clay fraction. Further clay minerals present in these soils may be of extremely low CEC or their interaction with hydrous oxides of Fe and Al would have modified the reaction complex to give very low negative charges. Ferric and Al oxides present in the clay occur as discrete crystals or coatings on layer silicates or other minerals and as mixed gels with colloidal silica and phosphates. These complexes are likely to play a direct role in buffering the CEC of the soils by blocking the negative sites (Deshpande et al., 1964 and Gast, 1977).

Al_o and Fe_o values are indicative of the amorphous forms of Fe and Al with very high specific surface and cation exchange capacity. Thus the highly positive corelations with CEC is well explained though their absolute content in the samples are very low. Decrease in CEC and increase in the senility of soils and advancement towards sesquioxide accumulation and ferrallitisation with decreased Fe_o and Al_o has been reported by many workers (Buringh 1970, Varghese 1981 and Byju 1989). The positive correlation with fluoride p^H (0.410) is due to its direct positive relation with Al_o and Fe_o, both giving significant correlation (0.703;0.682) with fluoride p^H. Further high fluoride p^H is indicative of soils with the mechanism of ligand exchange in operation. The fluoride ion can easily displace hydroxyls from the co-ordination shell of Al and Fe and probably gives a large increase in negative charge on the surface as the p^H of the solution rises (Wild, 1988).

The indirect negative effect of R_2O_3 was not sufficient to cause a substantial reduction in correlation coefficient between organic carbon and CEC. Al_2O_3 through its positive indirect effect has further influenced CEC probably through the interaction of Al with carboxyl and phenolic hydroxyl groups forming easily ionizable metal complexes (Schnitzer and Khan, 1978). However the metal complexes similarly formed with ferric iron is more stable and prone to lesser degree of ionization.

Clay content clearly indicated a positive direct effect (0.317) to CEC which was nullified and made negative by the indirect effects of R_2O_3 and organic carbon. Thus the effects of interaction of clay with organic matter and the dilution effects of R_2O_3 in masking the exchange sites are probably the main reasons for the highly negative correlation coefficient (-0.440). Interation of Al and Fe oxides and hydroxides with organic matter has been studied extensively. Humic colloids separated from acid soils often contain appreciable amounts of Al and ferric iron. Removal of Al from such colloids substantially increased the CEC by about 240 cmol Kg^{-1}. This according to Russell (1973) is presumably due to the presence of Al as a hydroxylated cation, such as $Al(OH)^{2+}$ or $Al(OH)^{+}{}_2$. Alternatively this could be due to aluminium ion forming a co-ordinate bond with carboxyl groups, and on this picture the greater the amount of Al present, the greater the proportion of humic particles held together. One could expect such interactions in the highly weathered variable charge soils also. Ferric ion complex with humic fractions behave in the same way as Al complexes. However dissociation of carboxylic group was difficult with Fe than with Al. Under field p^H conditions dissociation of Fe-complex was difficult than Al-complex and is not completely precipitated as the hydroxide until a high p^H has been reached (Russell, 1973). The aforementioned observations clearly explain the negative correlation of CEC with clay%, Al_2O_3%, Fe_2O_3% and R_2O_3%. According to Yagodin (1984) a substantial amount of ferric and aluminium oxides present occur as coatings on silicate clay minerals and as mixed gels which may also incorporate silica, phosphate and organic colloids. These interactions are also responsible for the strong negative effects of Al_2O_3, Fe_2O_3 and R_2O_3 on cation exchange capacity.

The influence of delta p^H on CEC was positive though not significant. The delta p^H values are invariably negative in all the samples studied. This indicates the very strong influence of organic matter in the soil in reducing the p^H through protonation and cation exchange and also due to the more sluggish deprotonation from the precipitated and aged sesquioxides and hydroxides. Mekaru and Uehara (1972), Sanchez (1976) and Bowden et al., (1980) have also reported similar observations based on studies conducted in variable charge soils of the tropics.

Out of the factors contributing negative charges discussed earlier nearly 55 percent of the variability is explained by the factors studied. A detailed investigation of the nature and stability of the clay-organic, clay- sesquioxide complexes formed over a range of p^H will throw additional information on this aspect and account for the remaining unknown factors.

1.2 Effect of charge contributing factors on anion exchange capacity.

Maximum positive correlation was obtained (0.615) with R_2O_3 and maximum negative correlation (-0.374) was observed in the case of organic carbon. The individual effects of Al_2O_3 and Fe_2O_3 were positive and significant inspite of negative direct effects, as brought out by very strong positive indirect effects. As the seat of positive charges are generally the broken edges of clay particles or the surfaces of the aluminium hydroxides, ferric hydroxides, goethite or other iron oxide films (Wild, 1988) a positive direct effect of sesquioxides and significant positive correlations with Al_2O_3, Fe_2O_3 and R_2O_3 are well explained.

The aluminium and iron hydroxides or oxide surfaces can hold anions by another process known as ligand adsorption (Wild,1988) particularly at low to medium p^H values as encountered in variable charge soils. As the field p^H in these soils are always below 5.5, positive charges that are likely to be generated through ligand exchange are more with larger amounts of Fe and Al oxides and sesquioxides. The significant negative correlation obtained between organic carbon and AEC is mostly due to the greater relative contribution of negative charges from the organic matter than the generation of positive charges. The direct role of dilution in the expression of positive point charges from hydrous oxides due to masking effect of organic matter cannot be ignored in these soils. Thus a decrease in the absolute positive sites contributed at high organic matter levels coupled with more positive sites created from sesquioxides at low organic matter levels are the major reasons for the negative relationships.

The positive effects of KCl-Al and fluoride p^H on AEC are indicative of the effects of high amounts of active aluminium and sesquioxides.

Of the thirteen important factors thus studied and discussed earlier nearly 48% of the variability alone is explained by the study indicating that AEC of the soils could not be fully explained by the above factors. Probably detailed investigations of the type of clay minerals, fractionation of the Fe and Al hydrous oxides and their interactions with organic colloids at various p^H levels may give a better explanation.

2. Potentiometric titrations

2.1 Zero point of charge (zpc)

The net electric charge and the zpc of soils as determined by potentiometric titrations are shown in Fig. 4 to 17 and appendix 1 to 14. In all the cases the zpc was displaced towards the acid side of the curve, from the zero point of titration. This is due to the presence of permanent negative charge balanced mainly by Al^{3+} ions (Van Raij and Peech,1972). The comparison of the values of the zpc for the two horizons within each profile indicates the influence of organic matter. As the mineralogical properties of these two selected horizons are more or less the same, the observed differences in electric charges and the zpc may be attributed to the organic matter. In all the seven profiles studied the effect of organic matter was to lower the zpc of the A_p horizons when compared to lower horizons.

In general it can be said that the presence of iron and aluminium oxides will tend to increase the zpc towards higher p^H values while the presence of clay minerals with permanent or structural negative charge as well as presence of organic matter will tend to shift the zpc of the soil to lower p^H values (Van Raij and Peech 1972). Thus the lower delta zpc between the surfce and sub-surface horizons observed inspite of considerable amounts of iron and aluminium oxides is due to the dominance of Kaolinite in the clay fraction and the influence of organic colloids combined with sesquioxides. Low zpc in sub-surface horizons has also been reported (Herbillon, 1988) and was found related to the presence of Kaolinite, which has a zpc of about 3. Thus soils with large amounts of Kaolinite clay minerals and low organic matter in the sub-surface horizons also exhibit lower zpc. Further the organo-mineral complexes formed are not much different between surface and sub-surface horizons of highly weathered Oxisols and Ultisols which are mostly depleted of bases and humus.

A large difference between the p^H determined in water and in 1N KCl indicate that the p^H of the studied soils is generally different from the zpc. This is further indicated in the figures 4 to 17 which show that for a given charge of any soil, the difference between the p^H measured in 1N and 0.001N NaCl is greater, the farther away from the zpc one select a point to make this comparison. This observation is in conformity with the studies made by Van Raij and Peech (1972). The distribution of net electric charge indicated that the magnitude of the charge is influenced by p^H as well as the concentration of NaCl. The titration curves are more or less similar to curves given for several metallic oxides and sesquioxide rich soils (Van Raij and Peech, 1972; Gallez et al, 1976; Laverdiere and Weaver, 1977; Mott, 1988) indicating that even for organic matter rich surface soils H^+ and OH^- are the potential determining ions.

Results shown here in figures (4 to 17) for the 7 selected Kerala soils and those reported by Van Raij and Peech (1972) and by Gallez et al (1976) for soils from Brazil and Nigeria confirm that the surface charge of Oxisols and Ultisols in the tropics generally follow the constant potential model although they contain considerable permanent negative charge. The zpc values of the surface and sub-soils measured in NaCl for all the selected Oxisols and Ultisols fall in the range of 3.5 to 4.1 indicating that the intense degree of chemical weathering undergone by these soils especially with regard to the degree of desilication is more or less the same. Thus zpc cannot be used as a taxonomic tool in classification to distinguish Oxisols from Ultisols (of Kerala).

2.2 Net charge as a function of surface potential and zpc

An attempt to predict the variation of electric charge of the samples with p^H and electrolyte concentration by the application of the double layer theory for a reversible interface has been made here. The net negative surface charge density of the selected samples was calculated as a function of surface potential and the results are plotted and presented in Fig. 18(a) to 19(b). The surface potential used in making the plots was calculated by the equation 1-(21). The experimental points for the net surface charge shown in this figure are the same as those given in Fig. 4 to 17. The surface charge used in constructing the curve labelled "Gouy-Chapman" was calculated directly by equation 1-(11) with suitable modifications by introducing constants so that $\sigma = 1.218 \times 10^{-7} c^{1/2}$ Sinh (0.0195ψ 0) where σ is given in cmol cm^{-2}, 'c' in gram ions L^{-1} and ψ 0 in millivolts.

A close scrutiny of the data and the Fig. indicate that the experimental values for the net surface charge are lower than those predicted by the Gouy-Chapman theory for the highest electrolyte concentration. The agreement improves with decreasing concentration of electrolytes and with increasing surface potential (Fig. 18(b)). However this trend is totally reversed as the concentration of electrolytes decreased further to 0.01 and 0.001.

Thus there is a critical concentration of the electrolyte below and above which the experimental values fail to obey the theoretical values of surface charge. The poorer agreement for the 0.01<u>N</u> and 0.001<u>N</u> electrolyte is not surprising since the determination of charge by potentiometric titration tacitly assumes the absence of H^+ and Al^{3+} as counter ions in the double layer, a condition not likely to be met at low electrolye concentrations, particularly in variable charge soils (Van Raij and Peech, 1972).

Calculation of the surface charge by the "Stern" model has not been attempted as it involved the simultaneous use of equations 1(12), 1(13), 1(14) and 1(15). Further application of these equations involved many assumptions which are not applicable to ordinary soil systems except under very precise laboratory conditions.

3. Effect of p^H, salt concentraftion and nature of electrolytes on charge characteristics.

3.1 p^H and concentration effect.

Table 9 represents the data on electric charges for the 8 soil samples, as determined by four methods of ion, adsorption measurement. The results indicate that both positive and negative charges co-exist in these soils. Thus the steric disposition of charges was such as to obviate complete cancellation of opposite charges. Figures 20 to 27 show that positive charges decrease and negative charges increase with increase in p^H. Samples of Kandiustult-B_2 of Pilicode, Paleustult-Bt_2 of Punalur and Haplustox-BA of Pachalloor exhibit net positive charge at p^H 3 for both (KCl and $CaCl_2$)the electrolytes. This effect vanished with a decrease in concentration of the electrolyte in the case of Kandiustult-B_2 and continued for lower concentration in the other cases. Upon decreasing the electrolyte concentration, however, the magnitude of both positive and negative charges decreased, as may be seen from the table and figures.

The p^H effect on positive and negative charges of soils is probably due to proton transfer mechanisms of organic matter, iron-aluminium oxides and edges of kaolinite (Morais et al., 1976 and Srivastava and Srivastava 1991) clay minerals. The existence of negative charges even at p^H3 is partially the result of a residual permanent negative charge arising from isomorphous substitution within the clay lattices. Differences in amounts of cations and anions adsorbed among the soils and between horizons of the same soil at a given p^H must be explained through differences in the quantities and characteristics of their exchange materials. Differences at high p^H values may be related to interactions between exchangeable aluminium, organic matter and mineral matter. At the lower p^H the differences may be due to some permanent charge occupied by hydroxy Al-ions which are released at the higher concentrations of KCl and $CaCl_2$ but not at lower concentrations.

In another set of four samples studied, relatively large variations in CEC_T, CEC_B and AEC was observed between p^H4 and 7 (Fig.: 36 to 39). Total CEC (CEC_T) and basic CEC (CEC_B) decreased drastically with decrease in p^H from 7 to 4, while significant generation of anion exchange sites was observed at low p^H. Both CEC_T and CEC_B estimated registered higher values than the corresponding values obtained for KCl and $CaCl_2$ in the above experiment. Thus the effect of p^H on surface charge is further confirmed in another set of estimations with a different p^H range.

The analysis of variance data obtained also showed (Tables 11 to 14) highly significant effect due to p^H and electrolyte concentration. The positive concentration effect of the index cations and anions is usually spectacular at extremes of p^H values. The concentration effect is explained by the compression of the double layer at higher concentrations and hence increased adsorption of the index cations and anions at the charge sites. This effect should be more for polyvalent cations and anions at equal concentrations and hence a critical concentration of the electrolyte is very important in deciding the charges determined.

On the contrary if a monovalent (1:1) electrolyte at very low concentration is used (NaCl, KCl) for the CEC estimation, the values obtained are likely to be more than the actual site charges since the hydrated ions with the intervening water hull does not permit a complete neutralization of charge through adsorption. Thus more number of hydrated ions will be adsorbed per unit of charge on the colloids.

3.2 The electrolyte effect

A critical study of the data presented in table 9 to 16 and Fig. 20 to 27 showed that at lower p^H values higher concentration of monovalent electrolyte registered higher values of CEC and AEC. At all p^H levels the higher concentration of KCl reported maximum CEC. No significant differences in CEC was seen at the two levels of $CaCl_2$ at $p^H 3$. At the highest p^H level the lowest concentration of both the electrolytes was equally effective, the maximum being estimated by $CaCl_2$. In all the instances the charge measured by KCl surpassed those obtained with $CaCl_2$. This is an unusual result and is probably due to the higher strength of KCl used and due to some kind of selectivity of the soil material for K. The decreasing order of the electrolyte efficiency in terms of the estimated values of CEC is $0.2\underline{N}$ KCl>$0.1\underline{N}$ Ca Cl_2>$0.05\underline{N}$ KCl>$0.01\underline{N}$ Ca Cl_2.

The analysis of variance showed significant individual effects due to p^H, electrolyte and soil and significant interaction effects (Table 11) due to soil x electrolyte, soil x p^H and electrolyte x p^H.

Similar results are obtained (table 14) for AEC also in all the soils used for the study. The decreasing order of electrolyte efficiency in terms of estimated AEC values is 0.2N KCl>0.1N Ca Cl_2>0.01N Ca Cl_2>0.05N KCl.

4. Evaluation of methods of ion-exchange measurements.

Data on ion exchange studies by different methods are summarised in table 17. Results show that CEC as estimated by the conventional neutral N NH_4OAc method in all soils give the highest values. The other six methods which might be considered to approach field conditions in all cases yield values much lower than those given by neutral N NH_4OAc. This is explained in equation 2 (1) by the hidden faults of the NH_4OAc method as it changes five important parameters that decide the charge on soil colloids. These are the dielectric constant (alcohol washing), salt concentration (1N which is totally unrealistic for soil solutions and changes to zero during washing), counter ion valence (use of monovalent NH_4^+ when dominant soil counter ions are divalent), zero point of charge (affected by organic acetate ion) and p^H (buffered at p^H 7). The effective CEC method though is suitable for routine laboratory analysis is not free from the defects of NH_4OAc, as it is assumed that all the cations extracted with NH_4OAc are exchangeable, and this might not be so under field conditions. Introduction of 1 M KCl to estimate exchangeable acidic cations in soils also have been questioned by Ameedee and Peech (1976) since it is not true for all highly weathered soils.

As against the expected theory of Gouy-Chapman, monovalent index cations K^+ and Na^+ from 0.2N KCl and Na Cl give slightly higher values than the compulsive exchange method and CEC_B particularly for the A_p and A_1 horizons. It is probably due to the higher concentration used when compared to other electrolytes employed in the study.

A strong relationship was found between CEC_T and ECEC showing that easily determinable exchangeable cations give a reliable estimate of total CEC at soil p^H. Also, CEC_B at soil p^H is more related to compulsive exchange CEC than the other methods.

Five methods were compared for anion exchange measurements. Anion exchange measurements by phosphate- adsorption method registered invariably higher values than compulsive exchange, chloride exchange by NaCl and 0.002 M $CaCl_2$. The highest mean value was recorded by 0.2 N KCl. A strong relationship was observed between compulsive exchange method and $CaCl_2$ method. The lowest value of all the methods was given by compulsive exchange method. The higher values recorded by methods M2 and M3 are probably due to the higher concentration of the electrolytes.

Phosphate adsorption is likely to give higher values particularly for the sub-surface horizons due to the possible adsorption and continued reaction that is expected with hydrous oxides of Fe and Al.

In all other methods chloride was the index anion which is known to be an indifferent ion and thus the differences in AEC measured was mainly due to differences in concentration of the electrolytes used.

T he analysis of variance data presented in Table 18 also showed significant difference due to various methods of ion exchange determinations. Compulsive exchange methods (M3) and CEC_B (M7) appeared to be equally effective and there was no significant difference between these two in CEC dêtermination. However NH_4OAc CEC and ECEC differed (M1and M2) significantly from the above two. Methods M4, M5 and M6 are also not significantly different from compulsive exchange, but registered higher values.

Among anion exchange measurements there was no significant difference between compulsive exchange (M1) and Ca Cl_2 method (M5). Other methods varied significantly from compulsive exchange method.

Thus compulsive exchange method appears to be much suitable for the combined determination of both CEC and AEC. Calcium chloride 0.002M, is found to be equally good (M7 in CEC and M5 in AEC measurements) for the combined estimation, but owing to simplicity of the procedure the former is preferred for soils containing mainly variable charge components like the Oxisols and Ultisols. There is now ample evidence to show that the traditional method is unsuited for ion exchange measurements in these soils due to the inherent defects of NH_4OAc discussed in the first paragraph of this chapter (Gillman 1979, Gillman and Sumner 1987). The compulsive exchange method is free of such criticisms and therefore would seem well suited for the Oxisols and Ultisols of Kerala.

5. Characterisation of permanent and p^H dependant charges.

The predominant variable charge nature of the clay systems of the soils studied are disturbed in the potentiometric titration curves. There is some uncertainty about the exact crossing point since the intercept does not coincide with the zero point of titration (Fig. 4,7,8,9,13,14,15,16 and 17). Thus the net electric charge is calculated with respect to the zpc rather than with respect to the zero point of titration. In all the samples the zero point of charge was found shifted towards the acid side of the curve. This observation indicated the presence of a permanent charge balanced mainly by Al^{3+} ions (Van Raij and Peech, 1972). Data on XRDA of all the samples studied also supported this view as the samples carried appreciable amounts of chloritized vermiculite along with Kaolinite (Gallez et al 1976, Laverdiere and Weaver 1977). The diffraction maxima for the clay minerals, however were indistinct or lacking entirely, prior to the removal of sesquioxides (XRD-pattern not shown) indicating that the sesquioxide constituent may be the more influencial component in regard to charge properties. During the pretreatment of samples for potentiometric titrations dissolution of appreciable amounts of sesquioxides probably might have exposed part of the permanent charge bearing components of the soil systems. Thus the highly weathered soils studied though carr~~ies~~y mainly variable charge components, from the electro-chemical point of view may be treated as mixed systems composed of constant potential surfaces with appreciable amounts of constant charge components.

The values of permanent charge determined by different methods are presented in table 19. Values obtained are negative in all the samples studied. A separate titration curve with p^H against the volume of acid/alkali added was constructed (not shown in the thesis) to locate the displacement of zero point of charge from zero point of titration and this shift in zpc was taken as the indirect measure of permanent charge.

The difference between cation exchange capacity and anion exchange capacity at zero point of charge (Gillman and Sumpter, 1986) was read from the curves of CEC and AEC versus p^H measured in two concentrations of KCl, (0.2N, 0.05N) and $CaCl_2$ (0.1N, 0.01N) to find out the permanent charge (Fig. 28-35). Similarly the curves of CEC_B, CEC_T and AEC versus p^H (Fig. 36-39) was also used to compute permanent negative charge in the same manner.

Permanent charge measured by K^+ and Cl^- adsorption (Gillman and Uehara, 1980) and obtained through theoretical calculations (Uehara and Gillman, 1980) resulted in comparable values with other methods, though the absolute values were slightly lower for the former two.

Thus the net surface charge density of the soils may be treated as the sum of the two types of surface charges, the variable charge and the permanent charge. Under field conditions the expression of the permanent charge component is minimum and the variable charge components such as Fe and Al oxides certainly play the most important role in influencing the electro-chemical properties. A better understanding of the electro-chemical behaviour of soils rich in hydrous oxides and Kaolinite thus will be helpful in the development of agro-techniques to alleviate the dilution effects of these low activity components in the generation of negative charges.

6. Contribution of Organic matter and Sesquioxides to exchange properties of soils.

To investigate the contribution of organic matter and sesquioxides to the exchange properties of organomineral complexes of surface and sub-surface horizons of seven profiles, this study has been undertaken. The results are presented in table 20 and 21.

In every instance of surface and sub-soils the CEC decreased substantially after peroxidation and the AEC registered marginal increase. There was no exception to this trend though the change in CEC and AEC consequent to peroxide treatment varied considerably. Decrease in CEC due to removal of organic matter is attributed to the predominantly high role of well decomposed organic matter in contributing functional groups to generate negative sites. However the degree to which various soil textural groups interacted with organic fractions varied from sample to sample and thus influenced differently the CEC after peroxidation. The increase in AEC of soils after peroxidation is mostly due to the release of predominantly positively charged finer particles of Fe, Al oxides previously held together by organic matter. As the relative abundance of negatively charged particles that are likely to be released in this manner is meagre in highly weathered soils, the net effect is an increase of the AEC. Further the stability of clay organic complexes also vary in soils with different physico-chemical properties.

When the data for all the soils were combined in a simple regression equation, about 64% (table 21) of the variability in CEC could be explained by the organic matter content alone. Partial regression equation of AEC on organic matter of the same soils indicated that only 8% of the AEC is contributed by organic matter.

In a manner analogous to the estimation of the net contribution of organic matter towards exchange properties, the net contribution of sesquioxides to ion exchange was estimated by DCB treatment of the samples. Consequent to sesquioxide removal the CEC increased slightly and the AEC decreased marginally. In the regression equation when the results of all the soil samples were combined, nearly 11% of the variability in CEC and 22% of the AEC could be explained by sesquioxide content. However the changes observed with respect to both CEC and AEC was not significant statistically. The non-significant effect as against the expected result may be due to the difference in the methodology adopted. For example the introduction of DCB and subsequent changes in p^H and ionic strength would have changed the exchange behaviour of the soil totally.

The combined effect of organic matter and R_2O_3 removal was significant with respect to CEC and AEC as evidenced from highly significant regression coefficients. Almost 59 and 50 percent of the CEC and AEC respectively was attributed by the combined effect of organic matter and R_2O_3. This clearly indicated that the combined interaction of organic matter and R_2O_3 with other soil components totally modified the exchange behaviour of soil colloids rather than their individual effects. The particular organomineral complex formed and the mechanism of their interaction to enhance both CEC and AEC needs elaboration and further investigation.

In summary, organic matter accounted for nearly 64% of the variation in CEC of the soils studied. The suspected dilution effect of R_2O_3 towards CEC and enhancement of AEC is not clearly brought out from the present study. The combined effects of organic matter and R_2O_3 interactions are to be investigated further for a clear understanding of the ion exchange behaviour of these highly weathered soils.

7. Mineralogical analysis of clay fraction.

7.1 X-ray diffraction analysis (XRDA).

The x-ray diffractograms obtained for the soil clays of the various profiles studied are presented in Fig. 40 to 46. When preferential orientation of the sample is used as was the case here, the flat crystals of the clay minerals tend to orient parallel to the glass slide. The diffraction from different planes is intensified improving the detectability of the diagnostic peaks of the clay minerals. The major clay mineral present was kaolinite as in indicated by the peak at 7.2 and 3.57 Å units. The sharpness of the peaks suggest well formed crystals.

For other minerals present the diagnostic peaks and the relative intensity are given in Table 22(a) and 22(b). Appreciable amounts of smectite group minerals were present in all samples except the Kandiustult of Arackal and Maruthur. However the effect was not reflected in the CEC. This probably is due to the fact that the hydrous oxides are adsorbed on the surface and or edges of the clay mineral particles as discrete colloidal particles which are often micro-crystalline. This considerably reduces the expression of point negative charges of the smectites. Goethite peaks are not sharp in the soils due to the removal of iron oxides during the pretreatment of the samples. Other minerals present in moderate amounts include vermiculite, chlorite, gibbsite, quartz, and feldspars.

There was considerable shifting of the base line of the diffractograms indicating the presence of amorphous minerals. This was observed in the Plinthustult of Pilathara, in the kandiustult of Pilicode, Paleustult of Punalur and in the Haplustult of Karakulam. This may be due to the decomposition of layer silicates, well ordered gibbsite and allophanes (Uehara and Gillman, 1981).

Glycol solvation and heating did not give much additional information. But the purpose of differentiating the smectite groups from other 2:1 layer silicates was achieved. In magnesium saturated samples smectite group was detected except in Haplustult of Karakulam. Appreciable amounts of mica was detected in Haplustox of Pachalloor, Kandiustult of Maruthur and in the Paleustult of Punalur. Presence of

Chlorite and vermiculite was confirmed in all the samples except the Kandiustult of Maruthur. Potassium saturation and heating at 550°C did not give any well ordered peak in the detectable range.

The results of mineralogical analysis show that Kaolinite is the most abundant mineral with lesser amounts of smectites quartz and gibbsite.

The highly weathered nature of the profiles and the movement of bases to lower layers suggest that there is intense chemical transformations at the sub-surface layers for the resynthesis of smectites. Therefore the smectite is either preferentially transported from the surface soils or formed in situ at lower layers by neoformations. The alkaline p^H conditions at moderate depth existed in the geological past coupled with solute movement and precipitation in these horizons must have created an environment for the re-synthesis of 2:1 type clay minerals. Similar conditions with the accumulation of silica, Al, Mg, Fe and alkaline environment leading to the resynthesis of smectites have been reported by Aba-Husayn et al (1980). Another explanation is that these soils are developed from granitic parent materials and the smectites formed are intermediates of the transformations of trace amounts of feldspars, chlorite and mica to kaolinite. These processes happened through geological ages and the relics of smectites formed are distributed at lower layers.

7.2 Scanning electron microscopic analysis

The SEM pictures of the clay samples from the different profiles are presented in plates 8 to 13. Scanning electron micrographs show a very diverse morphology of the soil clay minerals. The complexity of the morphological features is increased by the presence of organic matter, iron oxide and possibly amorphous material which have not been removed completely. A thick coating of iron oxide was found in all plates. Crystalline features were not visible even at very high magnifications (hence not photographed) due to thick oxide coating. Samples taken from the Paleustult of Punalur shows an abundance of organic matter coating over the clay materials. Not much additional information could be obtained from the SEM pictures of the samples. The core mineral is identified and confirmed as kaolinite by XRDA.

8. Surface area estimation

Data presented in table 23 indicated higher values for measured specific surface (EGME) than estimated values (negative adsorption data). Measured values varied from 49- 137 m^2g^{-1} whereas estimated values ranged from 32.91 to 108.64 m^2g^{-1}. The observed increase in measured surfce area may be due to multilayer adsorption of ethylene glycol over the soil particles. A close scruitny of the data revealed that the surface area of the samples measured clearly followed the organic matter content of the soil. The only exception to this trend is the Kandiustult of Arackal. The vertical increase in clay content with depth was not reflected in the surface area probably due to the dominant role played by organic matter. These observations are in conformity with the findings of Thompson et al.,(1989) who reported that 86% of the variability in specific surface could be explained by organic matter in fractionated soil materials. The micro-crystalline nature of the hydrous oxides and their coatings over the clay minerals may be one of the reasons for the non expression of the clay content increase in specific surface. The highest value recorded by both the methods was in the case of Paleustult A1,137 m^2 $g^{-1}$and 108.64m^2g^{-1} respectively for glycol retention and negative adsorption of chloride.

Specific surface determined by the two methods though not necessarily give an unequivocal value, the agreement in the trend is quite good for atleast three samples viz: Plinthustult of Pilathara, Paleustult of Punalur and the Haplustox of Pachalloor. The poor agreement in the trend for other samples between calculated and measured values cannot presently be explained.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

A study has been conducted on the electro-chemical properties of seven soils representing one Oxisol and 6 Ultisols of Kerala with a view to have a deeper insight in to their surface charge characteristics and mineralogy. The important observations and conclusions drawn from the investigations conducted are summarised below.

1. Path coefficient analysis of important charge contributing factors against parameters of charge measurement and the inter-relationships of all soil characters studied show that organic carbon %, clay %, R_2O_3%, Al_o% and Fe_o% are the major factors that control the surface charge behaviour of the soils. The thirteen factors studied explained nearly 55% and 48% of the variability of cation exchange and anion exchange respectively. Thus further detailed investigation is required to get additional information and to account for the remaining unknown factors of variability .

2. The net electric charge of samples was determined by potentiometric titration in the presence of varying concentration of NaCl. The potentiometric titration curves at four different ionic strengths of NaCl, crossed at the common point of intersection, the zero point of charge (zpc) , or the P^H at which the net electric charge was zero. The zpc for the surface horizons was found to be lower than the sub-surface horizons in all the soils studied. Soil to soil variation in zpc between surface and sub-surface horizons were more or less the same for all soils studied. Thus zpc cannot be recommended as a taxonomic tool in soil classification, to distinguish Oxisols from Ultisols.

3. The net surface charge density was found to vary with P^H and electrolyte concentration. Thus the electro-chemical behaviour of these soils was found to be similar to that exhibited by many oxides in which the surface potential of a reversible double layer is determined solely by the potential determining ions H^+ and OH^-.

4. A theoretical interpretation of the values for net surface charge and surface potential was made by the application of the double layer theory of Gouy-Chapman. The calculated and experimental values for net charge was found to be in agreement only at a critical concentration of the electrolyte. Below and above this concentration the experimental values of surface charge failed to obey the theory.

5. Positive and negative charges determined by the measurement of ion adsorption was found to vary with P^H, electrolyte concentration and valence of ions.

Thus a critical electrolyte concentration and P^H is very important in deciding the surface charge measurement. Any procedure developed for the measurement of electric charges in these soils will have to take into account the composition and ionic strength of the soil solution in order to relate the exchange capacity to actual field situation.

6. In a study for the evaluation of ion exchange measurements, it was found that the compulsive exchange method is most suitable for the combined estimation of CEC and AEC. Calcium Chloride 0.002 M was also found to be equally good, but owing to simplicity of the procedure, the former method appeared better. The traditional NH_4OAc method was found to give over estimations of CEC and thus very high values. The compulsive exchange method is free from the inherent defects of N NH_4OAc (P^H7) and hence would seem well suited for the Oxisols and Ultisols of Kerala.

7. Appreciable amounts of permanent charge was found in all soils studied though the samples were treated predominantly as variable charge systems. Values of permanent charge measured by different methods were found to be in good agreement with the estimated theoretical results. Under field conditions the expression of the permanent charge component was minimum and the variable charge components such as Fe, Al oxides certainly controlled the important electro-chemical properties.

8. In a separate experiment to find out the contribution of organic matter and sesquioxides to exchange properties of soils, it was found that 64 % of the CEC and 8% of the AEC was contributed from the organic matter. Sesquioxides could explain only 11% of the variability in CEC and 22% of the variability for AEC. The combined effect of organic matter and R_2O_3 removal was highly significant with respect to CEC and AEC in all samples studied. Almost 59 and 50 percent of the CEC and AEC respectively was attributed to the combined effect of organic matter and R_2O_3.

9. The results of mineralogical analysis show that kaolinite is the most abundant clay mineral present in the soil studied. Appreciable amounts of smectites, quartz and gibbsite was also identified. The presence of smectites was not reflected in the cation exchange capacity of any of the samples studied.

10. The SEM pictures of the samples studied showed a thick coating of iron oxide in all plates. Sample taken from the Paleustult of Punalur indicated the presence of organic matter occurring as coatings over clay materials.

11. The surface area of the samples measured closely followed the organic matter content of the soil. Vertical increase in clay content with depth observed in all the profiles was not reflected in the surface area. In general measured values of specific surface was much higher than the estimated values.

Thus the unique electro-chemical properties exhibited by these highly weathered soils are suggestive of special management packages. It will be of prime importance to conserve or even increase the organic matter status, because the contribution of negative charge from this source is vital to the retention of nutrient cations. Since these soils generally contain very little net negative charge in the sub-surface horizons, cations lost from the surface will be readily leached from the entire profile. On the other hand, even though anions might not be retained at the surface, they will be stored in the sub-surface horizons where positive charges are more prominent. Thus deep rooted crop plants could take advantage of this situation.

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APPENDICES

Appendix-1. Data derived from the potentiometric titration curves of the Kandiustult-Ap (Pilicode).

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		p^H	Net electric charge		Double layer
	H^+	OH^-		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	potential ψ_0 mV
1N	7.3	-	3.0	5.3	0.59	44.3
	4.8	-	3.3	2.8	0.31	27.0
	2.4	-	3.6	0.4	0.04	8.9
	-	2.4	5.0	-4.4	-0.49	-74.0
	-	4.8	6.2	-6.8	-0.75	-145.0
	-	7.3	7.3	-7.3	-1.03	-209.0
0.1N	7.2	-	2.9	5.2	0.58	50.2
	4.7	-	3.2	2.7	0.30	32.5
	2.3	-	3.6	0.3	0.03	8.9
	-	2.4	5.8	-4.4	-0.49	-121.2
	-	4.8	6.9	-6.8	-0.75	-186.2
	-	7.3	7.6	-9.3	-1.03	-227.5
0.01 N	7.1	-	2.8	5.1	0.57	56.2
	4.6	-	3.2	2.6	0.29	32.5
	2.2	-	3.5	0.2	0.02	14.8
	-	2.3	6.0	-4.3	-0.48	-132.9
	-	4.8	7.2	-6.8	-0.75	-203.9
	-	7.2	8.0	-9.2	-1.02	-251.2
0.001 N	7.1	-	2.8	5.1	0.57	56.2
	4.6	-	3.1	2.6	0.29	38.4
	2.2	-	3.5	0.2	0.02	14.8
	-	2.3	6.6	-4.3	-0.48	-168.4
	-	4.7	7.4	-6.7	-0.74	-215.7
	-	7.2	8.2	-9.2	-1.02	-262.9

Specific surface= 90 m^2 g^{-1}

zpc.2.cmol kg^{-1} acid side

Appendix-2. Data derived from the potentiometric titration curves of the Kandiustult-B_2 (Pilicode).

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		p^H	Net electric charge		Double layer
	H^+	OH^-		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	potential ψ0 mV
1N	7.3	-	3.1	5.7	0.84	53.2
	4.8	-	3.3	3.2	0.47	11.4
	2.4	-	3.8	0.8	0.12	11.8
	-	2.4	6.4	-4.0	-0.59	-141.8
	-	4.8	8.0	-6.4	-0.94	-236.4
	-	7.3	8.9	-8.9	-1.30	-289.6
0.1N	7.2	-	2.6	5.6	0.82	82.7
	4.2	-	3.1	3.1	0.45	53.2
	2.3	-	3.7	0.7	0.10	17.7
	-	2.4	6.8	-4.0	-0.59	-165.5
	-	4.8	8.4	-6.4	-0.94	-260.0
	-	7.3	9.2	-8.9	-1.30	-307.3
0.01N	7.1	-	2.5	5.5	0.80	88.6
	4.6	-	3.0	3.0	0.44	59.1
	2.2	-	3.6	0.6	0.08	23.6
	-	2.3	7.2	-3.9	-0.57	-189.1
	-	4.8	8.8	-6.4	-0.94	-283.6
	-	7.2	9.5	-8.9	-1.30	-325.0
0.001N	7.1	-	2.5	5.4	0.79	88.6
	4.6	-	3.1	3.0	0.44	53.2
	2.2	-	3.6	0.6	0.08	23.6
	-	2.3	7.7	-3.9	-0.57	-218.7
	-	4.7	9.2	-6.4	-0.94	-307.3
	-	7.2	9.7	-8.9	-1.30	-336.8

Specific surface ; 68.m^2g^{-1}

zpc. 1.6 cmolkg^{-1} acid side.

Appendix.3. Data dervied from the potentiometric titration curves of the Plinthustult-A_p (Pilathara)

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		p^H	*Net electric charge		Double layer
	H^+	OH^-		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	potential $\psi 0$ mV
1N	7.3	-	2.9	4.9	0.50	41.4
	4.8	-	3.3	2.4	0.24	17.7
	2.4	-	3.6	0.1	0.01	0.0
	-	2.4	5.2	-4.8	-0.48	-35.5
	-	4.8	6.2	-7.2	-0.73	-153.6
	-	7.3	7.3	-9.5	-0.96	-218.6
0.1N	7.2	-	2.8	4.8	0.49	47.3
	4.7	-	3.1	2.3	0.23	29.5
	2.3	-	3.6	-0.1	-0.01	0.0
	-	2.4	5.8	-4.8	-0.48	-130.0
	-	4.8	6.9	-7.2	-0.73	-195.0
	-	7.3	7.9	-9.7	-0.98	-254.1
0.01N	2.1	-	2.7	4.7	0.47	53.2
	4.6	-	3.1	2.2	0.22	29.5
	2.2	-	3.5	-0.2	-0.02	5.9
	-	2.3	6.1	-4.7	-0.47	-147.7
	-	4.8	7.4	-7.2	-0.73	-224.6
	-	7.2	8.2	-9.6	-0.97	-271.8
0.001N	7.1	-	2.6	4.7	0.47	59.1
	4.6	-	3.0	2.2	0.22	35.5
	2.2	-	3.5	-0.2	-0.02	5.9
	-	2.3	6.8	-4.7	-0.47	-189.1
	-	4.7	7.6	-7.1	-0.72	-236.4
	-	7.2	8.4	-9.6	-0.97	-283.6

Specific surface ; 98 m^2g^{-1}

zpc. 2.4 cmol kg^{-1} acid side

Appendix.4. Data dervied from the potentiometric titration curves of the Plinthustult-B_2 (Pilathara)

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		p^H	Net electric charge		Double layer
	H^+	OH^-		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	potential ψ0 mV
1N	7.3	-	3.3	5.0	0.63	29.5
	4.8	-	3.5	2.5	0.31	17.7
	2.4	-	3.7	0.1	0.01	5.9
	-	2.4	5.4	-4.7	-0.59	-94.6
	-	4.8	6.5	-7.1	-0.89	-159.6
	-	7.3	7.6	-9.6	-1.21	-224.6
0.1N	7.2	-	3.0	4.9	0.62	47.3
	4.7	-	3.3	2.5	0.31	29.5
	2.3	-	3.7	0.0	0.00	5.9
	-	2.4	5.9	-4.7	-0.59	-124.1
	-	4.8	6.8	-7.1	-0.89	-177.3
	-	7.3	8.2	-9.6	-1.23	-260.0
0.01N	7.1	-	3.0	4.8	0.61	47.3
	4.6	-	3.3	2.3	0.29	29.5
	2.2	-	3.6	-0.1	-0.01	11.8
	-	2.3	6.4	-4.6	-0.58	-153.7
	-	4.8	7.4	-7.1	-0.91	-212.8
	-	7.2	8.7	-9.5	-1.20	-289.6
0.001N	7.1	-	2.9	4.8	0.61	53.2
	4.6	-	3.3	2.3	0.29	29.5
	2.2	-	3.7	-0.1	-0.01	5.9
	-	2.3	6.8	-4.6	-0.58	-177.3
	-	4.7	7.9	-7.0	-0.89	-242.3
	-	7.2	8.9	-9.5	-1.21	-313.2

Specific surface; 79 m^2 g^{-1}

zpc; 2.3 cmol kg^{-1} acid side

Appendix.5. Data dervied from the potentiometric titration curves of the Paleustult - A_1 (Punalur).

Concentration of Nacl	Amount adsorbed cmol kg^{-1}		p^H	Net electric charge		Double layer potential ψo mV
	H^+	OH^-		cmol kg^{-1}	(cmol cm^{-2}) x 10^{-7}	
1N	7.1	-	3.3	4.7	0.34	17.7
	4.6	-	3.5	2.2	0.16	5.9
	2.1	-	3.7	-0.3	-0.02	-5.9
	-	2.4	4.9	-4.8	-0.35	-76.8
	-	4.7	5.5	-7.1	-0.51	-112.3
	-	7.2	6.0	-9.6	-0.70	-141.8
0.1N	7.2	-	3.4	4.8	0.35	11.8
	4.7	-	3.5	2.3	0.16	5.9
	2.2	-	3.8	-0.2	-0.01	-11.8
	-	2.4	5.2	-4.8	-0.35	-94.6
	-	4.8	6.2	-7.2	-0.52	-153.7
	-	7.3	6.6	-9.7	-0.70	-177.3
0.01N	7.3	-	3.3	4.9	0.35	17.7
	4.7	-	3.4	2.3	0.16	11.8
	2.3	-	3.7	-0.1	-0.01	-5.9
	-	2.4	6.0	-4.8	-0.35	-141.8
	-	4.8	6.8	-7.2	-0.52	-189.1
	-	7.4	7.2	-9.8	-0.71	-212.8
0.001N	7.4	-	3.3	5.0	0.36	17.7
	4.8	-	3.5	2.4	0.17	5.9
	2.4	-	3.7	0	0.00	-5.9
	-	2.4	6.3	-4.8	-0.35	-159.6
	-	4.7	6.9	-7.1	-0.51	-195.0
	-	7.3	7.4	-9.7	-0.70	-224.6

Specific surface; 137 m^2 g^{-1}

zpc ; 2.4 cmol kg^{-1} acid side

Appendix.6. Data dervied from the potentiometric titration curves of the Paleustult - Bt_2 (Punalur).

Concentration of Nacl	Amount adsorbed cmol kg^{-1}		p^H	Net electric charge		Double layer potential $\psi 0$ mV
	H^+	OH^-		cmol kg^{-1}	(cmol cm^{-2}) x 10^{-7}	
1N	7.3	-	2.7	4.8	0.72	65.0
	4.8	-	3.1	2.3	0.34	41.4
	2.3	-	3.6	-0.2	-0.03	11.8
	-	2.4	6.4	-4.9	-0.73	-153.7
	-	4.8	8.1	-7.3	-1.08	-254.1
	-	7.3	8.7	-9.8	-1.46	-289.6
0.1N	7.3	-	2.6	4.8	0.72	70.9
	4.7	-	3.2	2.2	0.32	35.5
	2.3	-	3.8	-0.2	-0.03	0.0
	-	2.4	6.3	-4.9	-0.73	-147.7
	-	4.9	8.5	-7.4	-1.10	-277.8
	-	7.4	9.3	-9.9	-1.47	-325.1
0.01N	7.4	-	2.9	4.8	0.72	53.2
	4.8	-	3.2	2.3	0.34	35.5
	2.3	-	3.8	-0.2	-0.03	0.0
	-	2.4	7.1	-4.9	-0.73	-195.0
	-	4.8	9.1	-7.3	-1.08	-313.2
	-	7.4	9.6	-9.9	-1.47	-360.5
0.001N	7.4	-	2.6	4.8	0.72	70.9
	4.9	-	3.2	2.4	0.35	35.5
	2.3	-	3.8	-0.2	-0.03	0.0
	-	2.4	7.3	-4.9	-0.73	-206.8
	-	4.9	9.1	-7.4	-1.10	-313.2
	-	7.4	9.8	-9.9	-1.47	-354.6

Specific surface : 67 m^2g^{-1}

zpc : 2.5 cmol kg^{-1} acid side

Appendix.7. Data dervied from the potentiometric titration curves of the Kandiustult-Ap (Arackal)

Concentration of NaCl	Amount adsorbed cmol kg^{-1}		p^H	Net electric charge		Double layer potential $\psi 0$ mV
	H^+	OH^-		cmol kg^{-1}	(cmol cm^{-2}) x 10^{-7}	
1N	7.3	-	2.9	5.2	0.75	35.5
	4.8	-	3.1	2.7	0.39	23.6
	2.3	-	3.6	0.2	0.03	-5.9
	-	2.4	5.4	-4.5	-0.65	-112.3
	-	4.9	6.5	-7.0	-1.01	-177.3
	-	7.4	7.6	-9.5	-1.37	-354.6
0.1N	7.4	-	2.8	5.3	0.76	41.4
	4.9	-	3.1	2.8	0.40	23.6
	2.4	-	3.5	0.3	0.04	0.0
	-	2.4	5.9	-4.5	-0.65	-141.8
	-	4.8	6.8	-6.9	-0.99	-195.0
	-	7.3	8.2	-9.4	-1.36	-277.8
0.01N	7.4	-	2.8	5.3	0.76	41.3
	4.9	-	3.1	2.8	0.40	23.6
	2.3	-	3.5	0.2	0.02	0.0
	-	2.4	5.9	-4.5	-0.65	-141.8
	-	4.9	7.4	-7.0	-1.01	-230.5
	-	7.4	8.7	-9.5	-1.37	-307.3
0.001N	7.3	-	2.8	5.2	0.75	41.4
	4.8	-	3.1	2.7	0.39	23.6
	2.4	-	3.6	0.2	0.03	-5.9
	-	2.4	6.8	-4.5	-0.65	195.0
	-	4.9	7.9	-7.0	-1.01	-260.0
	-	7.4	8.9	-9.5	-1.37	319.1

Specific surface ; 69 m^2g^{-1}

zpc ; 2.1 cmol kg^{-1} acid side

Appendix.8. Data dervied from the potentiometric titration curves of the Kandiustult-B_2 (Arackal).

Concentration of NaCl	Amount adsorbed cmol kg^{-1}		p^H	Net electric charge		Double layer potential $\Psi 0$ mV
	H^+	OH^-		cmol kg^{-1}	(cmol cm^{-2}) x 10^{-7}	
	7.4	-	3.0	4.9	0.69	47.3
	4.8	-	3.2	2.3	0.32	35.5
	2.3	-	3.7	-0.2	-0.03	-5.9
1N	-	2.3	4.9	-4.8	-0.67	-65.0
	-	4.8	5.8	-7.3	-1.03	-118.2
	-	7.3	7.1	-9.8	-1.38	-195.0
	7.3	-	2.9	4.8	0.67	53.2
	4.8	-	3.3	2.3	0.32	29.6
	2.4	-	3.8	-0.1	-0.01	0.0
0.1N	-	2.4	5.4	-4.9	-0.69	-94.6
	-	4.9	6.2	-7.4	-1.04	-141.8
	-	7.3	7.4	-9.8	-1.38	-212.8
	7.4	-	2.6	4.9	0.69	70.9
	4.8	-	3.2	2.3	0.32	35.5
	2.4	-	3.8	-0.1	-0.01	0.0
0.01N	-	2.4	5.9	-4.9	-0.69	-124.1
	-	4.9	7.8	-7.4	-1.04	-236.4
	-	7.4	8.7	-9.8	-1.38	-283.7
	7.4	-	2.7	4.9	0.69	65.0
	4.9	-	3.2	2.3	0.32	35.5
	2.4	-	3.8	-0.1	-0.01	0.0
0.001N	-	2.4	6.5	-4.9	-0.69	-159.6
	-	4.8	7.8	-7.3	-1.03	-236.4
	-	7.4	8.9	-9.8	-1.38	-301.4

Specific surface : 71 $m^2 g^{-1}$

zpc ; 2.5 cmol kg^{-1} acid side

Appendix 9. Data derived from the potentiometric titration curves of the Haplustult - Ap (Karakulam).

Concentration of NaCl	Amount adsorbed cmol Kg^{-1}		p^H	Net electric charge		Double layer potential
	H^+	OH^-		cmol kg^{-1}	(cmol cm^{-2}) x 10^{-7}	$\psi 0$ mV
1N	7.3	-	3.2	3.8	0.44	17.7
	4.7	-	3.4	1.2	0.14	5.9
	2.3	-	3.6	-1.2	-0.14	-5.9
	-	2.4	5.0	-5.9	-0.68	-88.6
	-	4.7	5.9	-8.2	-0.94	-141.8
	-	2.4	6.5	-10.9	-1.25	-117.3
0.1N	7.4	-	3.1	3.9	0.44	23.6
	4.8	-	3.4	1.3	0.15	5.9
	2.3	-	3.7	-1.2	-0.14	-11.8
	-	2.4	5.4	-5.9	-0.68	-112.3
	-	4.8	6.3	-8.3	-0.95	-165.5
	-	7.4	7.1	-10.9	-1.25	-212.8
0.01N	7.4	-	3.0	3.9	0.44	29.6
	4.8	-	3.2	1.3	0.15	17.7
	2.4	-	3.6	-1.1	-0.13	-5.9
	-	2.4	6.0	-5.9	-0.68	-147.7
	-	4.8	7.0	-8.3	-0.95	-206.8
	-	7.4	7.8	-10.9	-1.25	-254.1
0.001N	7.4	-	3.1	3.9	0.44	23.6
	4.9	-	3.3	1.4	0.16	11.8
	2.4	-	3.6	-1.1	-0.13	-5.9
	-	2.3	6.8	-5.8	-0.67	-135.9
	-	4.8	7.3	-8.3	-0.95	-224.6
	-	7.4	8.3	-10.9	-1.25	-283.7

Specific Surface 87 $m^2 g^{-1}$

zpc ; 3.5 cmol kg^{-1}, acid side.

Appendix 10. Data derived from the potentiometric titration curves of the Haplustult - B_2 (Karakulam).

Concentration of NaCl	Amount adsorbed cmol Kg^{-1}		p^H	Net electric charge		Double layer potential ψ0 mV
	H^+	OH^-		cmolkg^{-1}	(cmol cm^{-2}) x 10^{-7}	
1N	7.3	-	3.1	4.9	0.85	35.5
	4.7	-	3.3	2.3	0.04	23.6
	2.4	-	3.6	0.0	0.00	0.0
	-	2.3	4.8	-4.7	-0.82	-65.1
	-	4.8	5.6	-7.2	-1.20	-112.3
	-	7.3	6.5	-9.7	-1.70	-165.5
0.1N	7.4	-	3.0	5.0	0.87	41.4
	4.8	-	3.3	2.4	0.42	23.6
	2.4	-	3.7	0.0	0.00	0.0
	-	2.4	5.1	-4.8	-0.84	-82.7
	-	4.8	6.2	-7.2	-1.26	-88.6
	-	7.3	6.9	-9.7	-1.70	-189.1
0.01N	7.4	-	2.9	5.0	0.87	47.3
	4.9	-	3.2	2.5	0.43	29.6
	2.4	-	3.6	0.0	0.00	0.0
	-	2.4	5.8	-4.8	-0.84	-124.1
	-	4.8	6.8	-7.2	-1.26	-183.2
	-	7.4	7.8	-9.8	-1.72	-242.3
0.001N	7.4	-	2.8	5.0	0.88	53.2
	4.9	-	3.0	2.5	1.28	41.4
	2.4	-	3.6	0.0	0.00	5.9
	-	2.4	6.8	-4.8	-0.84	-183.2
	-	4.9	7.3	-7.3	-1.28	-212.8
	-	7.4	8.8	-9.8	-1.72	-301.4

Specific Surface 57 m^2g^{-1}

zpc ; 2.4 cmol kg^{-1}, acid side.

Appendix 11. Data derived from the potentiometric titration curves of the Kandiustult Ap (Maruthur).

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		p^H	Net electric charge		Double layer
	H^+	OH^-		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	potential $\psi 0$ mV
1N	7.3	-	2.8	4.9	0.58	53.2
	4.7	-	3.0	2.3	0.27	41.4
	2.4	-	3.4	0.0	0.00	17.7
	-	2.4	5.0	-4.8	-0.57	-76.8
	-	4.8	6.2	-7.2	-0.85	-147.8
	-	7.4	7.3	-9.8	-1.17	-212.7
0.1N	7.4	-	2.7	5.0	0.59	59.1
	4.8	-	3.1	2.4	0.28	35.5
	2.4	-	3.6	0.0	0.00	5.9
	-	2.4	5.2	-4.8	-0.57	-88.6
	-	4.8	6.4	-7.2	-0.85	-159.6
	-	7.4	7.8	-9.8	-1.12	-242.3
0.01N	7.4	-	2.6	5.0	0.59	65.0
	4.9	-	3.2	2.5	0.29	29.6
	2.4	-	3.6	0.0	0.00	5.9
	-	2.4	6.3	-4.8	-0.57	-153.7
	-	4.9	7.4	-7.3	-0.86	-218.7
	-	7.4	8.4	-9.8	-1.17	-277.8
0.001N	7.4	-	2.6	5.0	0.59	65.0
	4.9	-	3.1	2.5	0.29	35.5
	2.4	-	3.5	0	0.00	11.8
		2.4	6.8	-4.8	-0.57	-183.2
	-	4.9	7.6	-7.3	-0.86	-230.5
	-	7.4	8.4	-9.8	-1.17	-277.8

Specific Surface 84 m^2 g^{-1}

zpc; 2.4 cmol kg^{-1}, acid side.

Appendix 12 Data derived from the potentiometric titration curves of the Kandiustult - B_2 (Maruthur).

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		pH	Net electric charge		Double layer potential
	H^+	OH^-		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	$\psi0$ mV
1N	7.3	-	3.5	4.9	0.90	29.6
	4.7	-	3.7	2.3	0.42	17.7
	2.4	-	3.9	0.0	0.00	5.9
	-	2.4	5.2	-4.8	- 0.88	-70.9
	-	4.8	6.7	-7.2	- 1.33	-159.6
	-	7.3	7.3	-8.7	- 1.80	-195.0
0.1N	7.4	-	3.4	5.0	0.92	35.5
	4.8	-	3.7	2.4	0.44	17.7
	2.3	-	4.1	-0.1	-0.02	-5.9
	-	2.3	5.4	-4.7	-0.87	-82.7
	-	4.9	6.9	-7.3	-1.35	-171.4
	-	7.4	7.7	-9.8	-1.81	-218.7
0.01N	7.4	-	3.2	5.0	0.92	47.3
	4.9	-	3.6	2.3	0.46	23.6
	2.4	-	3.9	0.0	0.00	5.9
	-	2.4	6.5	-4.8	-0.88	-147.7
	-	4.8	7.5	-7.2	-1.33	-206.8
	-	7.4	8.3	-9.8	-1.81	-254.1
0.001N	7.4	-	3.2	5.0	0.92	47.3
	4.9	-	3.4	2.5	1.35	35.5
	2.4	-	3.9	0.0	0.00	5.9
	-	2.4	6.9	-4.8	-0.88	-171.4
	-	4.8	8.3	-7.2	-1.33	-254.1
	-	7.4	8.9	-9.8	-1.81	-289.6

Specific Surface : 54 m^2g^{-1}

zpc : 2.4 cmol kg^{-1}, acid side.

Appendix 13 Data derived from the potentiometric titration curves of the Haplustox -Ap (Pachalloor).

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		p^H	Net electric charge		Double layer
	H$^+$	OH$^-$		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	potential ψ0 mV
1N	7.3	-	3.2	5.1	0.56	41.4
	4.8	-	3.5	2.6	0.28	23.6
	2.3	-	3.8	0.1	0.01	5.9
	-	2.3	4.9	-4.5	-0.49	-59.1
	-	4.8	5.4	-7.0	-0.76	-88.7
	-	7.3	6.8	-9.5	-1.04	-171.4
0.1N	7.3	-	3.1	5.1	0.56	47.3
	4.9	-	3.4	2.7	0.29	29.6
	2.3	-	3.8	0.1	0.01	5.9
	-	2.3	5.9	-4.5	-0.49	-118.2
	-	4.8	6.8	-7.0	-0.76	-171.4
	-	7.4	7.6	-9.6	-1.05	-218.6
0.01N	7.4	-	3.0	5.2	0.57	53.2
	4.9	-	3.3	2.7	0.29	35.5
	2.4	-	3.6	0.2	0.02	17.7
	-	2.4	6.2	-4.6	-0.50	-135.9
	-	4.9	7.4	-7.1	-0.78	-206.9
	-	7.4	8.7	-9.6	-1.05	-283.7
0.001N	7.4	-	3.0	5.2	0.57	53.2
	4.9	-	3.4	2.7	0.29	29.6
	2.4	-	3.7	0.2	0.02	11.8
	-	2.4	6.5	-4.6	-0.50	-153.7
	-	4.9	7.6	-7.1	-0.78	-218.7
	-	7.4	8.6	-9.6	-1.05	-277.8

Specific Surface : 91 m^{2}g^{-1}

zpc ; 2.2 cmol kg^{-1}, acid side.

Appendix 14 Data derived from the potentiometric titration curves of the Haplustox -BA (Pachalloor).

Concentration of NaCl	Amount adsorbed (cmol kg^{-1})		p^H	Net electric charge		Double layer potential
	H^+	OH^-		(cmol kg^{-1})	(cmol cm^{-2})x 10^{-7}	ψ_0 mV
	7.3	-	3.5	5.0	1.02	29.6
1N	4.8	-	3.6	2.5	0.51	23.6
	2.4	-	3.9	0.1	0.02	5.9
	-	2.4	4.9	-4.7	-0.96	-53.2
	-	4.8	5.6	-7.1	-1.44	-94.6
	-	7.3	7.0	-9.6	-1.95	-177.3
	2.3	-	3.4	5.0	1.02	35.5
	4.8	-	3.6	2.5	0.51	23.6
0.1N	2.3	-	3.8	0.0	0.00	11.8
	-	2.4	5.9	-4.7	-0.96	-112.3
	-	4.8	6.9	-7.1	-1.44	-171.4
	-	7.4	7.8	-9.7	-1.97	-224.6
	7.4	-	3.2	5.1	1.04	47.3
0.01N	4.8	-	3.6	2.5	0.51	23.6
	2.4	-	3.8	0.1	0.02	11.8
	-	2.4	5.9	-4.7	-0.96	-112.3
	-	4.8	7.1	-7.1	-1.44	-183.2
	-	2.4	8.7	-9.7	-1.97	-277.8
	7.4	-	3.2	5.1	1.04	47.3
0.001N	4.8	-	3.6	2.5	0.51	23.6
	2.4	-	3.8	0.1	0.02	11.8
	-	2.4	6.5	-4.7	-0.96	-147.8
	-	4.9	7.9	-7.2	-1.46	-230.5
	-	7.4	8.9	-9.7	-1.97	-289.6

Specific Surface : 49 m^2 g^{-1}

zpc : 2.3 cmol kg^{-1}, acid side.

ELECTRO-CHEMICAL PROPERTIES OF SELECTED OXISOLS AND ULTISOLS OF KERALA WITH SPECIAL REFERENCE TO CHARGE CHARACTERISTICS AND SURFACE MINERALOGY

By

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ABSTRACT OF A THESIS

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ABSTRACT

A study has been conducted in seven selected profiles of Oxisols and Ultisols representing the important pedological units with a wide geographical distribution in the state to have a deeper insight into the electro-chemical behaviour of these soils. A multipronged approach to the studies made are highlighted to enable a clear understanding of the achievements as against the major objectives and approaches made.

A laboratory study with thirty six samples from seven profiles representing six Ultisols and one Oxisol has been carried out. Path coefficient analysis of important thirteen charge contributing factors against two parameters for measurement of charge and the inter-relationships of 15 soil characters show that organic matter, clay % , R_2O_3 %, Al_o% and Fe_o% are the major factors that control the surface charge behaviour of the soils. The factors studied explained only 55% and 48% of the variability of cation exchange and anion exchange respectively.

Study of the distribution of the electric charges in the surface and sub-surface horizons of the soils was made by means of potentiometric titrations and by measurement of adsorption of ions in the presence of varying concentration of electrolytes. The titration curves at different ionic strengths crossed at the common point of intersection, the zero-point of charge (zpc). Thus the electro-chemical behaviour of these soils was found to be similar to that exhibited by many metallic oxides in which the surface potential of a reversible double layer is determined solely by the activity of potential determining ions, H^+ and OH^- in the bulk of the solution. The zpc for the surface horizons was found to be lower than the sub- surface horizons in all the soils studied. Soil to soil variation in zpc between surface and sub-surface horizons were more or less the same for all samples. Thus zpc cannot be recommended as a taxonomic tool in soil classification to distinguish Oxisols from Ultisols.

From known values of surface area and zpc of these soils, the values for net electric charge was calculated by the application of the Gouy-Chapman model of double layer and was found to obey the theory only at a critical electrolyte concentration. As the soils were found to be similar to that of constant potential systems, the charge distribution varied substantially with P^H and electrolyte concentration. Direct measurement of adsorption of ions from solutions of KCl, NaCl and $CaCl_2$ showed that the nature and valence of index cations also influenced the magnitude of the negative charges on the soil particles. On the basis of the influence of P^H, electrolyte concentration and the valence of the counter-ions on the electric charges of the soils, most of the

conventional methods of ion- exchange determinations using buffered electrolytes at high concentrations appears to be inappropriate for tropical soils.

In a study for the evaluation of ion-exchange measurements it was found that the compulsive exchange method is most suitable for the combined estimation of CEC and AEC. The traditional ammonium acetate method was found to give over estimations of CEC and thus very high values. Calcium chloride 0.002 M was found to be equally effective but owing to the simplicity of the procedure, the former appeared better. The compulsive exchange method is free from the inherent defects of neutral normal ammonium acetate and hence would seem well suited for the Oxisols and Ultisols of Kerala.

Although sesquioxidic components in combination with organic matter apparently dominate the charge properties of these soils, there was evidence from the titration curves to show the presence of small amounts of clay minerals with permanent negative charge. This was confirmed by different methods and was found in good agreement with the estimated theoretical results. However under field conditions the expression of this constituent was minimum and the variable charge components such as Fe, Al oxides certainly control the electro-chemical characteristics.

In a separate experiment to find out the contribution of organic matter and sesquioxides towards exchange properties of soils, it was observed that about 64% of the negative sites and 8% of the positive sites was contributed from organic matter. Sesquioxides explained only 11% of the variability in CEC and 22% of the variability in AEC. The combined effect of organic matter and R_2O_3removal was highly significant with respect to CEC and AEC in all the soils studied.

Mineralogical investigation revealed the presence of kaolinite as the dominant clay mineral. Appreciable amounts of smectites, quartz and gibbsite was also identified. The presence of smectites was not reflected in the CEC of any of the samples. Scanning electron micrographs did not give much information other than the presence of a thick coating of iron oxide and amorphous materials over clay aggregates. The specific surface measured by ethylene glycol retention method invariably showed higher values than the estimated values obtained from negative adsorption data. The specific surface determined closely followed the organic matter content of the samples inspite of the vertical increase in clay content within profiles.