STUDIES ON EXCHANGE EQUILIBRIA AND ITS PREDICTION ON SOME ACID SOILS OF KERALA

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THESIS
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DECLARATION

I hereby declare that this thesis entitled "Studies on exchange equilibria and its prediction on some acid soils of Kerala" is a bonafide record of research 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 "Studies on exchange equilibria and its prediction on some acid soils of Kerala" is a record of research work done independently by Smt. SWARNAVI, S. under my guidance and supervision and that it has not previously formed the basis for the award of any degree, fellowship or associateship to her.

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INTRODUCTION

Cation exchange reactions have been described as the most important reaction in nature surpassed only by the photosynthetic reactions in green plants. Exchange studies are of importance in understanding and explaining many problems in soil science. It has long been recognized that many chemical and physical properties of soils are directly related to their exchange properties. Available plant nutrients, especially the cations, are those held on the exchange surface of soil colloids and released to the root surface or soil solution. Transport of cations, in relation to leaching loss of applied nutrients, is very much controlled by cation exchange phenomenon.

A thorough knowledge of the phenomenon of cation exchange equilibrium in soil is important in understanding the relative preference of the soil exchange complex, for a particular cation. It is equally important in predicting the cationic composition of the exchange complex from the concentration or activities of cations in soil solution.

Ever since the discovery of the cation exchange phenomena, efforts have been made to work out a formula to predict the equilibrium distribution of cations in solution and adsorbed phases of soil. A considerable portion of the plant nutrients present in the soil are held by the exchange complex, preventing leaching losses. Not only the amounts, but the ratios of cations in adsorbed phase or in the soil solution are of utmost importance in determining their behaviour in different soils. Expressions correlating equilibrium compositions of the exchange complex and the solution are important because they enable the prediction of changes in the adsorbed and solution phases in soil as influenced by fertilizer application, liming, ion uptake by plants, and addition of irrigation and waste water. Some published reports, however, suggest that besides cationic ratios, the factors like organic matter content in soil, total electrolyte concentration of the equilibrium solution and the nature of cations and anions considerably influence nutrient dissolution, adsorption, leaching in soils and ion uptake by plants. Approaches based on empirical, thermodynamic, and diffuse double layer theories have been used to describe the data on cation exchange equilibria.

The study of cation exchange equilibria involving Ca^{2+}, Mg^{2+}, Na^{+} could be useful in the prediction of leaching and accumulation of salt, closely associated with the process of sodification and desodification of normal and alkali soils respectively. On the other hand such a study of NH_4^+ and K^+ helps in understanding the behaviour of applied nitrogenous and potassic fertilizers as well as the release or fixation patterns of native and applied potassium. Cation exchange equilibria involving aluminium are of great importance to understand the phenomenon of nutrient leaching. A study on Ca-Al equilibrium in soils may be useful in correcting aluminium toxicity by liming.

Acid soils in high rainfall areas suffer from deficiency of nutrients and accumulation of aluminium on the adsorbed phase. More than 70 per cent of upland soils of Kerala are acidic. Soil acidity and loss of nutrient elements through leaching are probably among the major factors limiting more intense crop production.

Although aluminium is not an essential element, an appreciable amount of this element is often present in most plants. High aluminium levels in soil solution is known to cause direct harm to roots and decrease root growth and translocation of minerals especially calcium and phosphorus to the tops (Jarvis and Hatch, 1986). It is considered, an aluminium saturation of more than 20 per cent of the effective CEC of soils, as critical for many of the sensitive crop plants. Thus studies on the equilibrium of various cations in relation to aluminium have relevance in acid soil situations.

Organic matter apparently has some influence on the availability of aluminium. Recently organic compounds have been tried to prevent the dissolution of aluminium in acid soils instead of liming them. Addition of alfalfa meal has proved to decrease the toxic quantities of exchangeable aluminium in acid soils of pH 4-5.5. This was attributed primarily to complexing of exchangeable aluminium by organic matter. In this context the equilibrium in clay suspension between aluminium and other metallic cations has also been the subject of considerable research, because of the interest in acid neutralization and management of aluminium toxicity in acid soils.

It has been reported as early as 1961 (Nye et al), that soils and clays have strong preference for aluminium ions in dilute solutions. However, high salt concentration is generally capable of desorbing aluminium from these systems. Potassium has been found to be the most effective in displacing aluminium ions, from clays while Ca^{2+} has been found to be more weakly competitive with aluminium.

Pleysier et al. (1979) studied Al-K and Al-Ca exchange equilibria in an Ultisol profile and observed high selectivity of potassium to aluminium. The available guidelines on cation exchange equilibria in soils involving aluminium vis-a-vis, calcium, potassium or magnesium indicate that such informations are rather scanty for the acid soils of Kerala.

In view of the fundamental importance of such information, cation exchange equilibria involving aluminium were studied on some acid soils of Kerala differing in texture and organic matter with the following objectives.

1. The effect of different equivalent ion fractions of aluminium in the electrolyte solution on exchange equilibria in soils.

2. The influence of different cations on the free energy ($\triangle G^{o}$) and various selectivity coefficients for different soils.

3. The dependence of different exchange selectivity coefficients on potassium, calcium and magnesium saturation of soils.

4. Evaluation of the role of organic matter on cation exchange equilibria with special reference to potassium, calcium, magnesium and aluminium.

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

2.1. Studies on cation exchange in soils

Since the discovery of cation exchange in soils by Way (1849) efforts by various workers have thrown much light in this phenomenon. Marshall (1935) has aptly described cation exchange as the most important reaction in nature surpassed in fundamental importance only by the photosynthetic process in green plants. Donahue (1958) considers the cation exchange capacity of the soil to be a single index of fertility.

The cation exchange in soil was found to be influenced by a number of factors such as clay content, organic matter content, types of clay mineral, soil reaction etc. A brief review of the recent literature on the factors affecting cation exchange capacity, which are more relevant to the present investigation is presented.

2.1.1. Effect of clay and organic matter on cation exchange in soils

Since cation exchange is a surface phenomenon its rate will increase with increase in the amount of mineral and organic colloid.

Gopalaswami (1958) has reported a high CEC for the kari soils of Kerala, which was attributed to the high content of organic matter and illitic and montmorillonitic type of clay minerals present in them.

Wilding and Rutledge (1966) while investigating cation exchange capacity in a soil toposequence, found that in A horizons, organic matter contributed most to CEC, while in B horizons $<0.2\,\mu$ clay usually contributed most; $2 - 0.2\,\mu$ clay content was not usually significantly correlated with CEC in A or B horizons.

Feige (1970) found that decreasing levels of organic matter promote the sorption of potassium at the expense of that of calcium and magnesium. Rates of sodium, potassium, ammonium and magnesium sorption are rather low in comparison to calcium sorption, and further decrease with increasing cation saturation of the exchange complex. It is stressed that organic soils are capable of supplying, even in the presence of moderate nutrient reserve adequate amounts of plant available nutrients.

Satyanarayana et al (1970) determined the cation exchange capacity of specific gravity separates of sands and silts of basic regur soils. The separates with a specific gravity less than 2.35 had a cation exchange capacity of 80-90 me/100 g and contributed more than 60% to the cation exchange capacity of the whole fraction.

Syers et al (1970) observed a high correlation ($r = 0.96$) between CEC and oxidisable carbon, and a lower correlation ($r = 0.57$) between CEC and clay content. CEC of organic matter for all soils was 1.4 meq/g, and this value decreased from 1.64 meq/g in young soils to 1.22 meq/g in old soils. Peroxidation of surface samples caused a reduction in CEC. Reduced CEC of the clay fraction, that contained large amounts of amorphous material was apparently associated with blocking by organic matter of the negative charges of the clay components.

Wright and Foss (1972) studied the relative contribution of clay and organic matter to the CEC of Maryland soils. The average cation capacities of organic matter and clay from Ap horizons were calculated as 295 and 41 meq/100 g respectively. Standard partial regression coefficients indicated that organic matter was slightly more important than clay in predicting the CEC of surface horizons.

In a study of the cation exchange capacities of surface and subsurface soils of Afaka, Mokwa, Nimbia and Sanga River forest reserves in the Savanna region of Nigeria, Kadeba and

Benjaminsen (1976) found that the cation exchange properties of the surface soils were mostly associated with organic matter. Between 56 and 83 percent of the variation in the CEC values could be attributed to organic matter content. The exchange capacities of organic matter in the four reserves were calculated to be in the range 282-322 meg/100 g while those of clay were 7-18 meg/100 g.

In a study of the cation exchange capacity of some soil profiles of Kerala, Venugopal and Koshy (1976) found wide variations in the CEC of the different soil groups, the sandy soil recording the lowest and the black soil the highest value. With the exception of black, kari, and some alluvial soils all other groups had very low values. Correlation between CEC and clay was positive and highly significant. The relationship between CEC and organic matter was positive but not significant.

Bhatnagar et al (1977) reported that the cation exchange capacity of the Rajasthan canal soils showed a close correlation with clay, silt and organic matter content respectively. Clay had the predominant effect on CEC. This was followed in decreasing order by organic matter and silt.

While studying the cation exchange capacity of acid forest humus layers, Kaliz and Stone (1980) reported that organic matter was the chief source of exchange capacity at all localities studied.

Khanna et al. (1986) discussed the cation exchange characteristics of some acid organic-rich forest soils formed under sub-alpine eucalypt forest growing in the Australian capital Territory. Most of the exchange sites in the red and yellow earths studied are occupied by Aluminium and are associated with soil organic matter. Unbuffered salt solutions extract more Aluminium than could be associated with exchange sites so that the sum of cations in the extracts is an over estimate of effective cation exchange capacity.

2.1.2. Effect of type of clay mineral on cation exchange capacity in soil

In the case of red and laterite soils of Bihar, Lall (1953) obtained only relatively low values for CEC. The low CEC suggested that the principal clay mineral was kaolinite.

Menon and Mariakulandi (1957) observed that the low CEC of red soils of Tamil Nadu was due to the predominance of the kaolinite type of clay minerals.

Satyanarayana and Thomas (1962) have compared the chemical characteristics of Angadipuram and Kasaragod laterites. In both types of laterites, the exchange capacities were low and this was attributed to the kaolinite type of clay minerals present in them. The exchangeable Ca, Mg and K were found in traces in these soils.

Ovcharenko (1969) reported that ion-exchange constants decreased in the order Vermiculite > montmorillonite > palygorskite. Cation affinity for the different sorbents decreased in the order $Cu^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+} > NH_4^+$ Na^+. Substitution of inorganic exchange cations of montmorillonite and vermiculite by organic ones activated the inner surfaces of the minerals towards nonpolar solvents.

Martini (1970) observed a relatively high CEC value in recent volcanic soils (35.8 - 53.5 meq/100 g), and primarily related to organic matter. In latosols the CEC value is 37.1 meq/100 g, and is mostly due to the allophane and kaolinite types of clay minerals. Low cation exchange capacities tend to occur in older volcanic soils (12.5 meq/100 g) and are primarily related to clay (mostly kaolinite).

Martel et al (1978) reported that 50% of variations in cation exchange capacity of Gleysolic soils was caused by variation in mineralogy. The Alimodian clay is dominantly montmorillonite and has an average cation exchange capacity of 76.6 meq/100 g. The Bolinao clay has mixed clay mineralogy consisting of montmorillonite, vermiculite, poorly crystalline

1:1 type, some amorphous materials and gibbsite. Its CEC is 70.9 meq/100 g in the surface and 32.9 meq/100 g in the deep layer. The much lower value in the latter is due to "dilution effect" brought by relatively higher amounts of gibbsite in this subsoil. The Luisiania clay is kaolinitic, with a CEC of 31.2 meq/100 g in the surface. However, the deep layer (216 - 274 cm) has a higher CEC (72.2 meq/100 g) due to large amounts of high surface area amorphous aluminosilicates.

2.1.3. Effect of pH on cation exchange capacity of soils

Tamim et al (1975) reported that the cation exchange capacity of a soil with variable surface charge is pH dependent. When the pH of the plough layer was raised by applying $CaCO_3$, a substantial increase in the ability of the soil to retain cations (K, Mg and Ca) was noted due to the resultant increase in cation exchange capacity.

Bhangoo et al (1976) found that calcium saturation usually gave higher cation exchange capacity values than monovalent ion saturation.

Gessa and Mellis (1976) has observed an increase in the mean CEC of 24 soils from north eastern Sardinia with increasing soil pH, from 5.3 meq/100 g at pH3 to 14.9 meq/100 g at pH8. At pH3, 64% of the CEC was due to the clay fraction, but this decreased to 30% at pH 8; the contribution of the organic matter to the CEC increased from 30% at pH 3 to 67% at pH 8.

Khanna et al (1986) reported that CEC is not a unique property, but depends upon pH and ionic strength of the equilibriating solution. The exchange sites mainly carry negative charges of both permanent and variable nature. Higher carbon contents of soils are correlated with increase in CEC due to increasing ionic strength and with greater negative charge due to increasing pH.

2.2. Cation Exchange Equations

Ever since the discovery of the cation exchange phenomena, efforts have been made to work out a formula to predict the equilibrium distribution of cations in solution and adsorbed phases of soil. Three approaches, viz. thermodynamic, electric diffuse double layer theory, empirical and semi-empirical (statistical thermodynamics) are normally adopted in deriving equations to represent the distribution of ions between an exchanger and its equilibrium solution.

2.2.1. The thermodynamic approach

Assuming the system to consist of two distinct phases, ie. an exchange phase and a solution phase, the law of mass action can be applied. The process of action-exchange may be represented as the interchange of ions between the exchange phase and the solution phase as follows:

$$n_{Ae} \quad Ae + {}^{n_B}B \rightleftharpoons n_A A + n_{Be} Be \tag{1}$$

Where 'n' with subscripts 'A' and 'B' represents the number of reacting ions A and B, respectively; the subscript 'e' denotes ions in the exchange phase, while the absence of 'e' denotes ions in solution.

From classical thermodynamics, one has:

$$G = \bar{G}_i \; n_i$$

Where 'n' and $\bar{G}$ denote the number of moles and partial molar free energy, ie. chemical potential (μ), respectively. Introducing the definition of the ion activity 'a' as

$$\mu_i = \mu^o{}_i + RT \;\; \ln ai$$

and Gibbs free energy change during the reaction as

$$\Delta G = \leq \mu_i n_i \quad (\text{products}) - \leq \mu_i n_i \quad (\text{reactants})$$

one gets

$$G^o r = -RT \ln k \tag{2}$$

Where $K = a_A{}^{n^A} \; a_{Be}{}^{n^{Be}} / a_{Ae}{}^{n^{Ae}} \; a_B{}^{n^B}$ is the thermodynamic equilibrium constant; R, the universal gas constant; and T, the absolute temperature. The superscript 'o' denotes the standard state.

In Eq.(2), the standard Gibbs free energy of exchange is defined in terms of the equilibrium values of the activities of the reactants and products. Its value depends upon the standard state chosen for the different components. Hence Eq.(2) cannot be applied without further specifications. Babcock et al (1951) suggested the same standard state for both the ions on the exchange and in solution. This evidently amounts to G^o, and K = I. Since this choice of the standard state makes all the thermodynamic equilibrium constants equal to unity, it is less informative regarding the distribution of the cations.

For the interpretation of the experimental data on equilibrium between cations in solution and on clays, Gains and Thomas (1953) suggested that soils in homoionic state in equilibrium with infinitely dilute solutions of the salt of that cation are in their standard state. Babcock (1963), however, pointed out because of the hydrolysis of wweekly adsorbed cations at vanishing concentration, the adsorbed ions would no longer remain at unit mole fraction.

According to Bolt (1967), by the arbitrary choice of the standard state of the exchanger and the cations concerned, and this enables one to compare different cation pairs (and the same exchanger) or different exchangers (and the same cation pair).

Vanselow (1932) assumed that the exchanger phase could be treated in analogy with an ideal solid solution, according to which the activities of the adsorbed ions are set equal to their mole fractions 'M' in the exchanger phase. Argersinger et al (1950) extended Vanselow's theory to non-ideal exchanger and introduced activity coefficient 'f' for the adsorbed ions, defined as

$$f_i = a_{ie}/M_{ie}$$

The thermodynamic approach of Argersinger et al (1950), has been tried on clays and soil, systems by several workers (Diest and Talibudeen) (1967 a and 1967 b), Jensen ~~et al~~ and Babcock (1973), Poonia and Talibudeen (1977) etc.

The thermodynamic treatment enables one to know the relative preference of the exchanger for one cation over another. The changes in the composition of the exchange complex with respect to the changes in the equilibrium solution cannot be predicted on the basis of this treatment. Further, the activity coefficient of the adsorbed ions fail to give quantitatively the binding strength of a particular cation in absolute terms; they simply give the relative exchangeabilities of cations at their different degrees of exchanger saturation.

2.2.2. Electric Diffuse Double Layer Approach

It can be visualized that the presence of ions in the vicinity of a charged surface in soil may be either due to dissociation of ions from the surface under the influence of the polar water molecules and/or to the presence of soluble salts in the soil liquid phase. Whatever may be the reason for the ions to be present in the soil solution, these are under the influence of the two main forces, one being the cause of the other. The coulombic electrostatis force attracts and expels the counter-ions and co-ions, respectively, from near the charged surface and tends to bring the system to a state of minimum energy. A diffuse force then arises which while acting in opposition to the coulombic force tends to bring the system towards maximum entropy. The ultimate effect of these forces acting simultaneously, but in opposite directions, is the formation of the electric diffuse double layer of the ions near the charged surface, in which configuration the system has minimum free energy.

Using Poisson Boltzmann second order differential equation in one dimensional form for electrical diffuse double layer, Eriksson (1952) derived a relationship between mono-divalent cations in the equilibrium solution and mono-divalent cations in the diffuse double layer.

A simplified version of Eriksson's equation, as given by Bolt (1955), is

$$\frac{\Gamma 1}{\Gamma} = \frac{r}{\Gamma\sqrt{\beta}} \text{ Sinh }^{-1} \frac{\Gamma\sqrt{\beta}}{r + 4 \text{ Vc } \sqrt{C_2}}$$

Where Γ_1/Γ is the fraction of the surface charge neutralized by a monovalent cation; Γ the total surface charge density (meq cm^{-2}); β ($= \frac{8 \pi \quad F^2}{1000 \; \epsilon \quad RT}$) with F as the Faraday constant (2.892×10^{11} esu me^{-1}); R, the universal gas constant and Vc (= Cosh Yo) is related to the potential in the plane midway between the platelets,
$\gamma = C_1/\sqrt{C_2}$ (mole$^{1/2}$ litre$^{1/2}$)

The diffuse double layer approach, besides accounting for the preference of an exchanger for a particular cation, predicts the composition of an exchanger in equilibrium with a given solution. However, the strength and the weakness of this theory in the introduction of the surface charge density (ScD), which determines the preference of one cation over another.

2.2.3. Empirical Approach

The most extensively used empirical exchange equation dealing with cation exchange equilibria is due to Gapon (1933). Following the convention introduced by Gapon in specifying concentration (Co^+ and Co^{2+}) in mole $litre^{-1}$, this equation is written

as $$\gamma^+ / \gamma^{2+} = K_G \frac{Co^+}{Co^{2+}}$$

where γ^+ and γ^{2+} refer to monovalent and divalent cations on the exchanger and K_G is the Gapon constant.

Based on the experimental results on bentonite clay, soils and synthetic resins, Krishnamoorthy and Overstreet (1950) reported that Gapon equation was unsatisfactory/wholly inadequate for mono-divalent/mono-trivalent cation exchange.

Lagerwerff and Bolt (1959) tried to relate Eriksson's equation with the empirical approach of Gapon as under:

$$\frac{\gamma^+}{\gamma^{++}} = \frac{\frac{1}{\sqrt{\beta}} \ \mathrm{Sinh}^{-1} \ \frac{\Gamma \sqrt{B}}{\gamma + 4 \ Vc \quad a^{++}}}{\Gamma - \frac{\gamma}{\beta} \ \mathrm{Sinh}^{-1} \ \frac{\Gamma \sqrt{\beta}}{\gamma + 4 \ Vc \quad a_o^{++}}}$$

$$\text{Or} \quad \frac{\gamma^+}{\gamma^{++}} = K_\gamma$$

where $Y^{+} = S\Gamma_{+}$, $Y^{++} = S\Gamma_{++}$, with S as the specific surface area and $r = a_o^{+} / \sqrt{a_o^{++}}$, with a_o^{+} and a_o^{++} as the activities of monovalent and divalent cations in the equilibrium solution.

2.2.4. Statistical Thermodynamic Approach

The charge of the colloid may be due to substitution, dissociation of surface groups or the preferential a adsorption of anions. Then the charge may be associated with a particular adsorption site. This model, introduced by Davis (1950), Davis and Rible (1950); Krishnamoorthy et al (1949), and afterwards applied to exchange on soils, clays and resins by Krishnamoorthy and Overstreet (1950), is based on the assumptions that (1) the adsorbed ions are localized and one layer of ions would neutralize the surface charge (ii) the neighbouring ions have no influence on the interaction energy of an ion and the site, and (iii) the distance between the sites is large compared to the ionic size.

The generalized equation from this model, suggested by Krishnamoorthy et al (1949) and Davis (1950), is

$$K_D = \frac{M\,B_e^{\,nBe}}{M_{Ae}^{\,nAe}\,(\leq qi \quad M_i e)^{\,nBe-nAe}} \qquad \frac{a_A^{\,nA}}{a\,B^{nB}}$$

$$= \text{Constant}$$

Where 'q' is a parameter whose value depends on the valence of the ion and the assumed number of the nearest adsorption sites (Y), to the given adsorption site 'q_i' for any adsorbed ion 'i' of valence 'Z' is given by:

$$q_i = \frac{Y \cdot Z_i - 2\,Z_i + 2}{Y} \qquad Z_i - \frac{2\,Z_i}{Y} + \frac{2}{Y}$$

Various exchange equations may be derived from the above generalized equation by assigning different values to Y. For Y = 2, ie. linear array of surface charges, $q_i = 1$, then

$$K_D = \frac{a_A^{nA} \; M_{Be}^{nBe}}{a_B^{nB} \; M_{Ae}^{nAe}} = \text{Constant} = Kv$$

where Kv = Vanselow constant.

Bloksma (1956) pointed out that in selecting a hexagonal array (Y = 6) of surface charges, there are eight adjacent sites for a divalent ion; two of these sites give the value of $q^{++} = 4/3$, rather than 5/3.

Hence,

$$K_D = \frac{a^{++}}{a^{+2}} \quad \frac{M^{+2}}{M^{++}\,(M^{+} + 1.6\,M^{++})} = \text{Constant.}$$

An attempt was made by Heald et al (1964) to develop a semi-empirical approach to predict exchangeable cations, considering the distribution of adsorbed ions over the Stern and the Gouy parts of the diffuse double layer.

The purely empirical and semi-empirical or statistical thermodynamic approaches propounded to explain the experimental results are free from involved mathematical considerations/assumptions and are simple to use. They not only give the relative preference of a cation by an exchanger (based on selectivity quotients) but can also predict the changes in the cationic composition of the exchanger.

2.3. Studies on cation exchange equilibria in soils

The equilibrium in clay suspension between aluminium and other metallic cations has been the subject of considerable study because of the interest in acid neutralization and aluminium toxicity in acid soils. The study of cation exchange equilibria involving Ca^{2+} Mg^{2+} and Na^{+} could be useful in the prediction of leaching and accumulation of salts closely associated with the processes of sodification and desodification of normal and alkali soils, respectively. On the other hand, such a study of K^{+} helps in understanding the behaviour of applied potassic fertilizers, as well as the release/fixation patterns of native and applied potassium.

2.3.1. Exchange equilibria of Aluminium versus different cations

Coulter and Talibudeen (1969) from a study of K-Al exchange equilibria in clay minerals and acid soils, showed that Al^{3+} was strongly preferred to K^+.

Singh and Talibudeen (1971) studied the K-Al exchange thermodynamically for nine acid soils of Malaya. In seven soils K was adsorbed more strongly than Al. The activity coefficient of adsorbed K (fk) increased, then decreased with decreasing K saturation. The activity coefficient of Al (fAl) decreased with decreasing Al saturation. Between soils fk changed much more than fAl. with saturation changes.

Cation exchange equilibria in an acid ultisol profile involving K-Al, Ca-Al, K-Ca, Na-K and Na-Ca exchanges were studied by Pleysier et al (1979). They observed a high selectivity of K to Al. The overall selectivity sequence follows the order of K $>$ Al $>$ Ca $\simeq$ Na.

Baruah et al (1983a) studied Al-Ca, Al-K and Al-NH_4 exchange equilibria in some acid soils of Assam. The normalised exchange isotherm indicated the order of preference for the competing cations Al $>$ Ca $>$ NH_4 $>$ K, whereas the values of free energy changes showed the order NH_4 $>$ K $>$ Al $>$ Ca.

The higher thermodynamic preference to NH_4 and K over Al was ascribed to significant content of dioctahedral mica together with vermiculite and smectite.

2.3.2. Exchange equilibria of calcium versus different cations

Hunsaker and Pratt (1971), while studying the Ca-Mg exchange equilibria in soils, found that a hydroxy-aluminium coated montmorillonite clay had a higher preference for Ca than the original clay. Allophane, an organic soil and soils containing amorphous minerals or Kaolinite plus gibbsite all showed higher preference for calcium than is expected in montmorillonite clays and soils.

The effects of $MgCl_2$ - $CaCl_2$ and $MgCl_2$ - $Cacl_2$ - NaCl salt systems of different Mg:Ca ratio on a sodium dominant bentonite clay were studied (Mondal, 1972) in the presence or absence of Kankar (impure $CaCO_3$ occurring in some soils). Exchangeable calcium on the bentonite increased at all Mg:Ca ratios. It further increased in the presence of Kankar, following the release of calcium. The original ESP of the clay was reduced considerably when suspended in both $MgCl_2$ - $CaCl_2$ and $MgCl_2$ - $CaCl_2$ - $NaCl_2$ systems, the reduction was greater in the presence of Kankar.

Krishnappa et al (1974), while studying the Ca-Mg exchange equilibria in three soils of Karnataka, observed that Ca was preferentially adsorbed by a red sandy loam, a black clay soil and a laterite sandy clay loam. The laterite showed a strong preference for calcium but only a slight preference was shown by the black soil.

Udo (1978) studied the thermodynamics of K-Ca and Mg-Ca exchange reactions on a kaolinitic soil clay. For the K-Ca system, the selectivity coefficients were high indicating a greater affinity of the clay for K than for Ca. The high equilibrium constant and the negative values of standard free energy and the enthalpy changes for the exchange of Ca for K also revealed a preference of the clay for K^+ relative to Ca^{2+}. In the Mg-Ca system, the exchange isotherms and low selectivity coefficients indicated a preference of calcium for the clay. This exchange of Ca for Mg was accompanied by an increase in the free energy and enthalpy changes also pointing to a more stable Ca-clay than Mg-clay.

Bladel and Gheji (1980) reported that Ca was selectively adsorbed over Mg. Affinity for Ca over Na or Mg ions was greatest in the calcareous soils and varied approximately in the same order as the soil organic matter content. In the Ca-Na system, the selectivity coefficient was rather independent of ionic strength. Enthalpy and entropy changes were negative for the substitution of Ca by Na. These results indicate that the preference of Ca was probably due to overall entropy change.

Baligar (1984), from his studies on the influence of calcium and magnesium on the ionic equilibria and selectivity of cations in soils, showed that addition of calcium (Ca) and magnesium (Mg) reduced the fractional saturation of monovalent cations in solution and exchange phase. However, no such conclusion could be drawn for divalent cations. In all the soils Rubidium was preferentially adsorbed over K and Na. In all the soils, increasing levels of Ca and Mg reduced the magnitude of selectivity coefficient for homovalent ion pairs (Rb/Na, K/Na) and mono-divalent ion pairs (Rb/Ca, Rb/Mg, K/Ca, K/Mg, Na/Ca, Na/Mg). These changes in selectivity coefficients are attributed to fractional saturation changes on the exchanger and differences in the free energy of hydration of the two counter ions involved.

2.3.3. Exchange equilibria of potassium versus different cations

Studies on the ion exchange equilibria and selectivity characteristics of the soils of Tarai region (U.P.) revealed that these soils had higher selectivity of K than to other cations (Na, Ca, Ba and Al), and Mg was preferentially adsorbed over calcium. The higher K-selectivity of these soils was due to their higher micaceous mineral content, whereas the preference for Mg was attributed to the presence of vermiculite material (Raju and Raman, 1978).

Perrott (1981) studied the K-Mg cation exchange selectivity of some allophanic soil clays, imogolite and a range of synthetic hydrous oxides and amorphous aluminosilicates. The preference of the aluminosilicate for Mg^{2+} increased with pH. Hydrous oxides of iron and aluminium were found to specifically adsorb Mg^{2+} at alkaline pH values.

Exchange equilibria of K versus Ca+Mg on samples of eight soils derived from alluvial were studied by Singh et al (1981). The specificity of the exchange sites for K^+ decreased first abruptly and then gradually with increasing potassium adsorption ratio (PAR) of the equilibrium solution. The normalized exchange isotherms showed that at low exchangeable potassium percentage (EPP) the equivalent fraction of K^+ on the exchange complex were greater than that in the equilibrium solution, whereas the reverse was true at high EPP.

In their studies on the exchange equilibrium of K versus Ca and Na in soils from semiarid regions of India, Mehta et al (1983) observed a higher specificity for K^+ to Ca^{2+} in the first 50-70% K^+ saturation. In the K^+- Na^+

system the specificity for K^+ to Na^+ was, however, higher for the whole range of exchange isotherms. The soils high in organic carbon had higher preference for K^+ than low in organic carbon. The values of the standard free energy change of the exchange reactions for $K^+- Ca^{2+}$ and $K^+- Na^+$ systems were negative for all the three soils tested. These values were, however, more negative for $K^+- Na^+$ than for $K^+- Ca^{2+}$ systems, suggesting higher preference for K^+ in the former.

Goulding and Talibudeen (1984) reported that residual fertilizer potassium and farm yard manure residues decreased preference for K in soils from the Broadbalk and Saxmundham Rotation I Experiments, but more so at Broadbalk than at Saxmundham, presumably because of greater duration and amount of potassium manuring at Broadbalk. Farm yard manure had a very complex effect on the exchange characteristics of Broadbalk soils.

While investigating the thermodynamics of potassium exchange in calcium saturated soils, Jardine and Sparks (1984[a,b]) observed a preference for K at low values of N_K (molefraction of K in solution) and for calcium at higher values. This selectivity reversal may be attributed to exchange sites of varying reactivity for K and Ca ions and supports the hypothesis of the multireactive nature of the soil. Although potassium was selectively bound at low N_K, the soil exhibited an overall calcium preference as noted by the positive standard free energy values. The strong binding of K ions with some sites of the soil was associated with the presence of vermiculite clay minerals.

In 14 Indian soils, the changes in ionic equilibria, selectivity coefficients and rate of diffusion coefficient for K, Na, Ca and Mg were investigated by Baligar (1985). All soils had a greater fraction of Ca and Mg on the exchange phase than in solution, whereas with K and Na the reverse was found. Potassium adsorption isotherms for all the soils differed, indicating the difference in the nature of soil materials involved. Chalmers soil with a high clay content with a high CEC had high differential buffer values for K. In all the soils K was adsorbed preferentially to Na at all the levels of K addition. Calcium was adsorbed preferentially to Mg on Zaneville and Toronto soils. However, in Chalmers and Raub soils the reverse was observed when the level of K addition exceeded 1 and 0.5 meq/100 g soil respectively.

A laboratory experiment was conducted (Mehta et al 1986) to study the K - Ca exchange equilibria in some soils from semi-arid regions of India. In light textured and relatively low potassium soils, about 50% of the exchange sites preferred K; this figure was reduced drastically to about 5%, upon fixed K depletion. The values of the standard free energy change of the exchange reaction, $\triangle G°$, were negative in all the soils and decreased with depletion of fixed K, indicating the reduced specificities for K. The Gapon selectivity coefficient, K_G, decreased with increased K saturation. None of the selectivity coefficient tested remained constant throughout the exchange isotherm.

In their studies on the effect of organic matter on potassium-calcium exchange in soils, Poonia et al (1986 a) observed a higher apparent K specificity in the first 40-50% potassium saturation. Farm yard manure treatments resulted in a small but consistent increase in the shift of isotherms towards a greater K-preference; the shift being more conspicuous in the low K-saturation zone. The standard free energies of K - Ca exchange ($\triangle G°$) were strongly negative suggesting strong preference for K over Ca in these soils.

Poonia et al (1986 b) reported that application of farm yard manure caused a small but consistent increase in the preference of K over Mg. The calculated standard free energy of K-Mg exchange was strongly negative, suggesting a strong thermodynamic preference for K over Mg. All the selectivity quotients scrutinized were strongly K saturation dependent, the dependence becoming more pronounced with the addition of farm yard manure.

2.3.4. Exchange equilibria of sodium versus different cations

Poonia et al (1980 a) studied sodium-calcium exchange as affected by total electrolyte concentration at different sodium adsorption ratios of the equilibriating solutions on some soils of Haryana. The normalized exchange isotherms for sodium revealed that at a given proportion of sodium: calcium the accumulation of sodium in the adsorbed phase increased with the increase in total electrolyte concentration, which was in accordance with ratio law equation. The values of ΔG° Na-Ca increased and that of K_G decreased with the increase in total electrolyte concentration, thereby showing an increase in the preference of calcium by the soil exchanger with increase in total electrolyte concentration at given sodium adsorption ratio.

Poonia et al (1980 b) studied sodium-calcium and sodium-magnesium exchange equilibria in soils to compare the roles of natural and applied organic matter. Their observation was that 'apparently' the applied organic matter had a greater preference for divalent cations than the natural organic matter in soils. They attributed this to incomplete oxidation of the chemically more active natural organic matter by hydrogen peroxide treatment and long term binding action of natural organic matter in the clay humus complex.

Al-Chalabi and Pasricha (1981) studied sodium-calcium exchange equilibria in some salt affected soils. The relationship between exchangeable sodium ratio (ESR) and sodium adsorption ratio (SAR) was used for the graphical estimation of equilibrium SAR for 3 saline sodic soils. One of the soils showed a steeper slope of the ESR-SAR exchange isotherm indicating a higher affinity for sodium than the other two soils.

Sheta et al (1981) observed that the Gapon selectivity coefficient, K_G, increased linearly with the exchangeable calcium fraction (or decreased with ESP), thereby showing an increase in the preference of Ca^{2+} by the soil (Nile Delta soil) with increase in exchangeable calcium.

Baruah et al (1983b) studied the sodium-calcium and sodium-potassium exchange equilibria in three illite dominated soils of semi-arid region. In Ca-Na system, the exchange isotherms of sodium lay below the diagonal and the values of Gibbs free energy change (ΔG°) were positive, indicating higher preference of Ca to Na by the soil exchanger. The activity coefficients of the adsorbed sodium were higher than those of calcium. The values of Gapon coefficient (K_G), Vanselow coefficient (Kv) and Krishnamoorthy-Davis-Overstreet (K_{KDO}) increased with sodium saturation. In Na-K system the shape and position of the exchange isotherms of sodium and the sign and magnitude of ΔG° suggested considerably higher preference for K to Na.

Fletcher Philip et al (1984 a) studied ternary exchange reaction (involving Na, Ca, and Mg) on a montmorillonitic soil and concluded the preferential adsorption of calcium. This preference was attributed primarily to the presence of organic matter associated with the soil separate. However, the exchange isotherms showed no effect of pH in the range between five and Seven 7, and no effect of exchangeable sodium percentage in the range between zero and 25%.

The binary cation exchange process, Na → Ca, Na → Mg and Ca → Mg were investigated for a montmorillonitic soil (Fletcher Philip et al., 1984 b). The exchange isotherm indicated some preference on the soil for calcium and magnesium over sodium and for calcium over magnesium.

Sposito and Le Vesque (1985), while investigating the binary and ternary cation exchange reaction involving sodium, calcium and magnesium, observed a preferential adsorption of Ca and Mg over Na by the clay minerals, and for calcium over magnesium in the binary exchange. The principal ternary exchange data, on the other hand, indicated no selectivity difference between Ca and Mg in the presence of adsorbed sodium at a nominal exchangeable sodium percentage of 25.

MATERIALS AND METHODS

MATERIALS AND METHODS

An investigation was carried out to study the exchange equilibria involving Al-K, Al-Ca and Al-Mg systems in some acid soils of Kerala, differing in their texture and organic matter content.

3.1. Collection of soil samples

Three soil types namely Kari, Laterite and Redloam were selected to represent the acid soils of Kerala. Several surface soil samples (0-20 cm. depth) in bulk were collected, so as to get three levels of organic matter within each soil type. The locations of collection are given below:-

Sl. No.	Location	Order	Local name	Texture	Organic matter
1.	Karthikapally	Entisol	Kari	Clay	High
2.	Ambalapuzha	Entisol	Kari	Clay	Medium
3.	Karthikapally	Entisol	Kari	Clay	Low
4.	Palode	Oxisol	Laterite	Sandy clay	High
5.	Chullimanoor	Oxisol	Laterite	Sandy clay	Medium
6.	Karakulam	Oxisol	Laterite	Sandy clay	Low
7.	Vellayani	Alfisol	Redloam	Sandy clay loam	High
8.	Vellayani	Alfisol	Redloam	Sandy clay loam	Medium
9.	Vellayani	Alfisol	Redloam	Sandy clay loam	Low

The soils were air dried in shade and ground with a wooden mallet. Each sample was then screened through a 2 mm. sieve and the screenings were collected and stored in labelled, stoppered glass bottles. The preliminary analysis of soil was carried out by adopting standard analytical procedures and the values are given in Table 1.

3.2. Preliminary analysis of soil

3.2.1. pH

pH of the soil in 1:2.5 soil water suspension was determined using the glass electrode of Perkin-Elmer pH meter.

5.2.2. Electrical conductivity

Conductivity of 1:2.5 soil water extracts was determined using a solu-bridge.

3.2.3. Organic carbon

Organic carbon was estimated by the Walkley and Black's rapid titration method as given by Jackson (1967).

3.2.4. Cation exchange capacity

Cation exchange capacity was determined by using neutral normal ammonium acetate method (Jackson, 1967).

3.2.5. Exchangeable cations

Exchangeable potassium was extracted by ammonium acetate (Jackson, 1967) and determined by the flame emission using EEL flame photometer.

Exchangeable calcium and magnesium were estimated from ammonium acetate leachate by titration with EDTA (Hesse, 1971).

Exchangeable aluminium was extracted with one normal KCl solution (Hesse, 1971) and determined in PE-3030 Atomic Absorption Spectrophotometer.

3.2.6. Specific surface area

The specific surface area of the soil samples were determined using ethylene glycol adsorption method (Bower and Goertzen, 1959).

3.2.7. Surface charge density

Surface charge density (SCD) was determined from specific surface area (S) using the formula,

$$\text{CEC} \quad \text{C mol } (+)\ \text{Kg}^{-1} = 10^{6}\ \text{S}\ (\text{m}^{2}/\text{g}) \times \text{SCD}\ (\text{meq}/\text{m}^{2})$$

3.2.8. Particle size distribution

The mechanical analysis of the sample was carried out by Bouyoucos hydrometer method.

3.3. Experimental details

To conduct cation exchange equilibrium studies each of the sample was made homoionic with potassium, magnesium and calcium for the K+Al, Mg+Al and Ca+Al systems, respectively. The homoionic samples were then air dried and used for the equilibrium studies.

3.3.1. Preparation of homoionic soil

Generally the use of homoionic soils/clays was preferred to conduct the cation exchange equilibrium studies. This is because of the experimental convenience and accuracy in the estimation of cation pairs involved.

The soil samples (100 g) were made homoionic with K for K-Al, with Mg for Mg-Al system, and with Ca for Ca-Al system. This was done by repeated washings with one normal chloride solutions of potassium, magnesium or calcium as the case may be in 1:5 soil solution ratio using the leaching technique. The homoionic form of the soil was ensured by ascertaining the absence of other cations in the leachate. The samples were made salt free by two successive washings with distilled water, four washings with 95% ethonol and finally tested with Ag NO_3 for chloride free leachate.

Table 1. Physicochemical properties of the soils.

Properties	Kari Soil			Laterite Soil			Red loam Soil		
	1	2	3	4	5	6	7	8	9
pH 1:2.5	3.40	3.20	3.20	5.20	5.00	4.90	5.40	6.30	6.30
EC 1:2.5 T.S.S. (dSm^{-1})	0.05	0.05	0.05	0.15	0.15	0.20	0.30	0.30	0.30
CEC C mol (+) Kg^{-1}	38.00	20.20	15.40	23.60	16.40	11.40	16.20	13.80	9.20
Specific surface area (m^2/g)	82.20	71.53	38.20	57.31	40.71	27.32	33.12	29.83	18.92
Surface charge density (me/cm^2 x 10^7)	1.10	1.18	1.50	1.25	1.60	2.15	1.63	1.74	1.92
Organic carbon (%)	6.67	3.49	1.06	3.55	2.05	1.20	3.16	1.89	0.81
Organic matter (%)	12.02	6.02	1.83	6.12	3.53	2.07	5.45	3.26	1.40
Exchangeable cations C mol (+) Kg^{-1}									
Ca	8.50	5.80	3.48	5.83	4.94	3.23	3.13	4.92	3.10
Mg	3.31	2.14	1.16	1.59	1.32	1.90	2.92	1.25	0.86
K	0.98	0.87	0.81	0.65	0.35	0.22	0.49	0.81	0.95
Al	2.32	1.54	1.48	1.32	1.07	0.89	1.08	0.94	0.63

Table 1 contd.

Properties	Kari Soil			Laterite Soil			Red loam Soil		
	1	2	3	4	5	6	7	8	9
Particle size distribution									
Coarse sand (%)	6.25	8.64	15.41	28.06	36.38	38.93	38.45	37.21	43.36
Fine sand (%)	7.13	10.84	13.76	15.32	17.39	16.83	16.70	22.43	23.24
Silt (%)	16.40	17.80	20.80	12.30	7.40	9.57	8.80	6.30	3.80
Clay (%)	58.20	56.70	48.20	38.20	35.30	32.60	30.6	30.8	28.20
Texture	Clay	Clay	Clay	Sandy clay	Sandy clay	Sandy clay	Sandy clay loam	Sandy clay loam	Sandy clay loam

3.3.2. Equilibriation procedure

2.5 g of each of the potassium, magnesium and calcium saturated homoionic soils were equilibriated with 25 ml chloride solutions (1:10 soil solution) of K+Al, Mg+Al and Ca+Al respectively at ten different equivalent ion fractions of Aluminium, viz. 0.01, 0.05, 0.075, 0.1, 0.2, 0.3, 0.4, 0.5, 0.75 and 1.0 at a total electrolyte concentration of 20 me/litre for each ion pair. All the treatments were taken in duplicate. The suspensions were equilibriated for 24 hours with intermittent shaking, at room temperature.

3.3.3. Estimation of equilibrium exchangeable cations

The estimation of cations on the exchange complex was carried out using the following method. The soil with the equilibrium solution was filtered through Whatman No. 42 filter paper. In the filtrate Ca and Mg were determined by Versenate titration, K flamephotometrically and Al in PE-3030 Atomic Absorption Spectrophotometer. The exchangeable cations were obtained from the depletion/increase in the amounts of competing cations in the original solution after equilibriation.

3.3.4. Prediction of cation exchange equilibria in soil

Experimental data of cation exchange equilibria studies was explained using thermodynamic and empirical approaches.

3.3.4.1. Thermodynamic approach

Thermodynamic treatment as proposed by Gaines and Thomas (1953) was used to describe the results of the investigation. In thermodynamic approach, assuming the system to consist of two distinct phases, an exchange phase and solution phase, the law of mass action can be applied.

In this approach following equations were used to calculate (1) thermodynamic equilibrium coefficient (K_N), (2) thermodynamic exchange constant (K), (3) standard free energy change of the exchange reaction (ΔG^o). For the cation exchange reaction

$$Z_B Ax + Z_A B \rightleftharpoons Z_A Bx + Z_B A$$

where x is the exchanger. A is original cation on the exchanger. B is replacing cation. Z_A and Z_B are the valencies of cations A & B respectively.

(1) Thermodynamic equilibrium coefficient (K_N)

$$K_N = \frac{(N_B)^{Z_A}}{(N_A)^{Z_B}} \times \frac{(a_A)^{Z_B}}{(a_B)^{Z_A}}$$

'N' stands for equivalent fraction of cations on the adsorbed phase and 'a' for the activity of cations (mol/litre) in the equilibrium solution. Activity (a) = Concentration (C, mol/l) x activity coefficient (r).

The activity coefficients of cations in the equilibrium solution was calculated by using the modified Debye-Huckle equation as under

$$\log r_i = - \frac{A\, Z_i^2 \sqrt{I}}{1 + \alpha \beta \sqrt{I}}$$

A and β are constants, their values depend on temperature end dielectric constant of the medium, is the radius of the hydrated ion; and I is the ionic strength (mol/litre) of the solution and can be calculated as under

$I = 0.5 \sum C_i Z_i^2$ where C is the ionic molar concentration; and Z, the valency of the ion.

(2) Thermodynamic exchange constant (K)

Thermodynamic exchange constant was calculated by using the relationship

$$\ln K = -(Zb - Za) + \int_0^1 \ln Kc \, dN_B$$

where K is the thermodynamic equilibrium constant.

(3) Change in free energy (ΔG^o)

$$\Delta G^o = - RT \ln K$$

where R is gas constant (Cal deg^{-1} $mole^{-1}$)

T is Kelvin temperature

ΔG^o is the approximate Gåbb's free energy

(4) Normalized exchange isotherm

Whether a particular cation is preferentially adsorbed to another in an exchange reaction was also seen from the shape of the normalized exchange isotherm. Normalized exchange isotherm is the graph between the equivalent fraction of a cation on the exchange versus its equivalent fraction in equilibrium solution. The diagonal indicate that both the cations are equally preferred on the exchange complex.

3.3.4.2. Empirical approach

The purely empirical and semi-emperical or statistical thermodynamic approaches not only give the relative preference of a cation by an exchanger (based on selectivity coefficients) but can also predict the changes in the cationic composition of the exchanger.

The following empirical equations given by various workers were used to calculate the selectivity coefficients.

$$(1)\quad K_V = \frac{(M_B)^{Z_A}}{(M_A)^{Z_B}} \times \frac{(a_A)^{Z_B}}{(a_B)^{Z_A}} \quad \text{.......... (Vanselow, 1932)}$$

$$(2)\quad K_G = \frac{N_B}{N_A} \times \frac{(a_A)^{1/Z_A}}{(a_B)^{1/Z_B}} \quad \text{.......... (Gapon, 1933)}$$

$$(3)\quad K_{KDO} = \frac{(M_B)^{Z_A}}{(M_A)^{Z_B}\,(UM_B + MA)} \times \frac{(a_A)^{Z_B}}{(a_B)^{Z_A}}$$

(Krishnamoorthy et al, 1948)

Where a_A and a_B are the activities (mol/l) of cations A and B in the equilibrium solution respectively, N_A and N_B are the equivalent fractions, and M_A and M_B are the mole fractions of cations A and B on the adsorbed phase, respectively, $U = 2(Y-1)/Y$ with Y as the number of exchange sites influencing a given site. For calculation it was taken that $Y = 4$ or $U = 1.5$.

3.3.5. Statistical analysis of the data

After computing the various selectivity coefficients a correlation study was conducted to find out the dependency of these selectivity coefficients on exchangeable potassium, calcium and magnesium percentage.

RESULTS

RESULTS

Expressions correlating equilibrium compositions of the exchange complex and the solution are important, because they enable the prediction of changes in the adsorbed and solution phases in soil as influenced by fertilizer application, addition of irrigation and waste waters, ion uptake by plants etc. In the present study experiments were conducted to find out 1. The effect of different electrolyte concentrations on exchange equilibrium in soil solution and adsorbed phase 2. The influence of different cations on the free energy and various selectivity coefficients for different soils.

The cation exchange equilibrium study was carried out for aluminium-potassium system, aluminium-calcium system and aluminium-magnesium system, and the results are given in Tables 2-23 and interpreted in Figures 1-18.

4.1. Aluminium-Potassium system

4.1.1. Effect of different electrolyte concentrations and organic matter levels on aluminium-potassium exchange

Table 2 presents the data on the equilibrium concentrations of aluminium and potassium for kari soils. In

Table 2 Equilibrium concentration of aluminium (Al) and potassium (K) for K^{+}- Al^{3+} system in kari soils

Sl. No.	Soil 1				Soil 2				Soil 3			
	q_{Al} Cmol(+) kg^{-1}	CAl (me l^{-1})	q_K Cmol(+) kg^{-1}	CK (me l^{-1})	q_{Al} Cmol (+) kg^{-1}	CAl (me l^{-1})	q_K Cmol (+) kg^{-1}	CK (me l^{-1})	q_{Al} Cmol (+) kg^{-1})	CAl (me l^{-1})	q_K Cmol (+) kg^{-1})	CK (me l^{-1})
1	0.18	0.02	37.82	19.98	0.16	0.04	20.04	19.96	0.14	0.06	15.26	19.94
2	0.88	0.12	37.12	19.88	0.82	0.18	19.38	19.82	0.81	0.19	14.59	19.81
3	1.28	0.22	36.72	19.78	1.13	0.37	19.07	19.63	1.02	0.48	14.38	19.52
4	1.48	0.52	36.52	19.48	1.24	0.76	18.96	19.24	1.17	0.83	14.23	19.17
5	3.11	0.89	34.89	19.11	2.97	1.03	17.23	18.97	2.28	1.72	13.12	18.28
6	4.99	1.01	33.01	18.99	4.32	1.68	15.88	18.32	3.23	2.76	12.17	17.24
7	6.89	1.11	31.11	18.89	5.89	2.11	14.31	17.89	4.77	3.23	11.28	16.12
8	8.21	1.79	29.79	18.21	7.47	2.53	12.73	17.47	5.86	4.14	9.54	15.86
9	12.49	2.51	25.51	17.49	9.69	5.31	10.51	14.69	8.01	6.99	7.39	13.01
10	16.41	3.59	21.59	16.41	11.60	8.40	8.60	11.60	9.39	10.61	6.01	9.39

q - adsorbed phase

C - solution phase

Table 3 Equilibrium concentration of aluminium (Al) and potassium (K) for K^+- Al^{3+} system in laterite soils

	Soil 4				Soil 5				Soil 6			
Sl. No.	q_{Al} Cmol (+) kg^{-1}	CAl (me l^{-1})	q_K Cmol (+) kg^{-1}	CK (me l^{-1})	q_{Al} Cmol (+) kg^{-1})	CAl (me l^{-1})	q_K Cmol (+) kg^{-1})	CK (me l^{-1})	q_{Al} Cmol (+) kg^{-1}	CAl (me l^{-1})	q_K Cmol (+) kg^{-1}	CK (me l^{-1})
1	0.16	0.04	23.44	19.96	0.16	0.04	16.24	19.96	0.16	0.04	11.24	19.96
2	0.87	0.13	22.73	19.87	0.78	0.25	15.65	19.75	0.74	0.96	10.68	19.74
3	1.26	0.24	22.34	19.76	1.02	0.48	15.38	19.52	0.98	0.52	10.42	19.48
4	1.37	0.63	22.23	19.37	1.23	0.77	15.17	19.23	1.09	0.91	10.31	19.09
5	2.89	1.11	20.71	18.89	2.50	1.50	13.90	18.50	2.14	1.86	9.26	18.14
6	4.41	1.59	19.19	18.41	3.87	2.13	12.53	17.87	3.21	2.79	8.19	17.21
7	6.14	1.86	17.46	18.14	5.12	2.88	11.28	17.12	4.22	3.78	7.18	16.22
8	7.92	2.08	15.68	17.92	6.89	3.11	9.51	16.89	5.64	4.36	5.76	15.64
9	11.74	3.26	11.84	16.74	9.34	5.66	7.06	13.34	7.74	7.26	3.66	12.74
10	15.14	4.81	8.41	15.14	11.61	8.39	4.79	11.61	9.14	10.86	2.66	9.41

q - adsorbed phase

C - solution phase

Table 4 Equilibrium concentration of aluminium (Al) and potassium (K) for K^{+}- Al^{3+} system in redloam soils

Sl. No.	Soil 7				Soil 8				Soil 9			
	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_K (Cmol (+) kg^{-1})	CK (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_K (Cmol (+) kg^{-1})	CK (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_K (Cmol (+) kg^{-1})	CK (me l^{-1})
1	0.18	0.02	16.02	19.98	0.16	0.04	13.64	19.96	0.15	0.05	9.05	19.95
2	0.88	0.12	15.32	19.88	0.76	0.24	13.04	19.76	0.71	0.29	8.49	19.71
3	1.31	0.19	14.89	19.81	1.18	0.32	12.62	19.68	0.94	0.56	8.26	19.44
4	1.71	0.29	14.49	19.71	1.21	0.79	12.59	19.21	1.08	0.92	8.12	19.08
5	3.08	0.92	13.12	19.08	2.55	1.45	11.25	18.55	2.16	1.84	7.04	18.16
6	4.02	1.98	12.18	18.02	3.70	2.30	10.11	17.70	3.08	2.92	6.12	17.08
7	5.52	2.48	10.68	17.52	4.98	3.02	8.82	16.98	4.21	3.79	4.99	16.21
8	6.83	3.17	9.37	16.83	6.23	3.77	7.57	16.23	5.12	4.88	4.08	15.12
9	9.54	5.46	6.66	14.54	8.53	6.47	5.27	13.53	6.46	8.54	2.74	11.46
10	10.04	8.23	6.16	11.77	10.49	9.51	3.31	10.49	7.18	12.82	2.02	7.18

q - adsorbed phase

C - solution phase

general, for all the three soils (1, 2 and 3) with increase in the concentration of aluminium in the equilibriating solution, more of aluminium was adsorbed into the soil exchanger. When the equivalent fraction of aluminium in the equilibriating solution was increased from 0.01 to 1.00, the increase in exchangeable aluminium was from 0.18 to 16.41 Cmol(+) kg^{-1} for soil 1, 0.16 to 11.6 Cmol(+) kg^{-1} for soil 2 and 0.14 to 9.39 Cmol(+) kg^{-1} for soil 3. From Table 2 it is also clear that soil 1 with high organic matter released more soil potassium into the equilibriating solution compared to soil 2 (with medium organic matter) and soil 3 (with low organic matter).

A similar trend was observed for laterite and redloam soils (Tables 3 and 4). Among the laterite soils the adsorption of aluminium was maximum for soil 4 (with high organic matter), followed by soil 5 and 6 with medium and low organic matter respectively (Table 3). For the maximum equivalent fraction of aluminium (1.00) in the equilibriating solution the quantity of aluminium adsorbed was 15.14 Cmol(+) kg^{-1} for soil 4 as against 11.61 and 9.14 Cmol(+) kg^{-1} for soil 5 and 6 respectively.

Among the redloam soils, soil 7 with high organic matter adsorbed 10.04 Cmol(+) kg^{-1} of aluminium as against

10.49 and 7.18 Cmol(+) kg^{-1} for soils 8 and 9, respectively (Table 4). As in the case of kari and laterite soils, here also the adsorption of aluminium increased with increase in the concentration of aluminium in the equilibriating solution. Generally the adsorption of aluminium and release of potassium increased with increase in the level of organic matter in the three soil types.

4.1.2. Exchange isotherms

The normalized exchange isotherms, depicting a relationship between the equivalent fractions of Al^{3+} in equilibrium solution, ${}^{C}\mathrm{Al}/\mathrm{Co}$ (where ${}^{C}\mathrm{Al}$ is the concentration of Al^{3+} in me/l, and Co is the total electrolyte concentration in me/l) and in the adsorbed phase, ${}^{q}\mathrm{Al}/{}^{q}\mathrm{o}$ (where ${}^{q}\mathrm{Al}$ is the concentration of Al^{3+} in me/100 g, and ${}^{q}\mathrm{o}$ is the cation exchange capacity in me/100 g) for kari, laterite and red-loam soils are given in Figures 1, 2 and 3, respectively. In all the three soil types the isotherms lay above the diagonal, showing thereby the preferential adsorption of aluminium to potassium.

From Fig.1 it is clear that there is only slight difference in the specificities of soil one and two for aluminium. Soil three with low organic matter showed the minimum preference for aluminium.

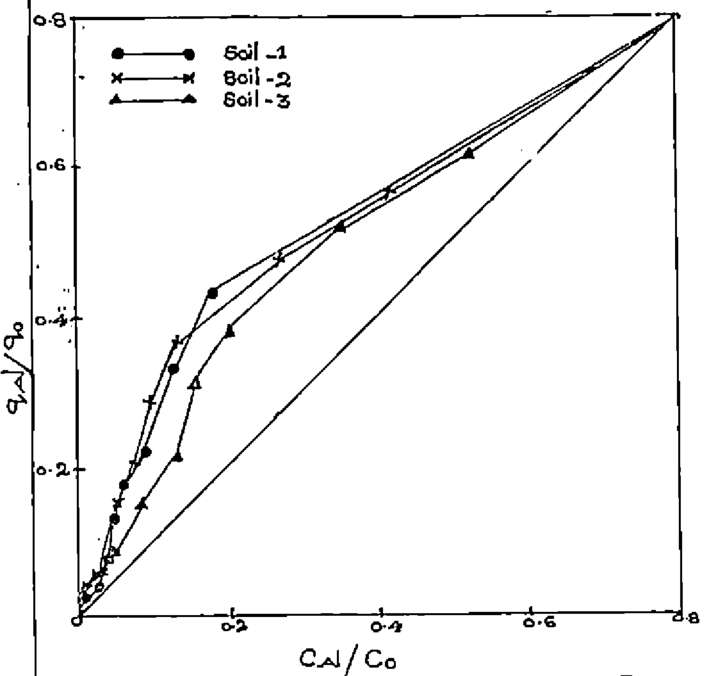

Fig.1 Normalized exchange isotherms of Al^{3+} for K^+-Al^{3+} system in karisoils

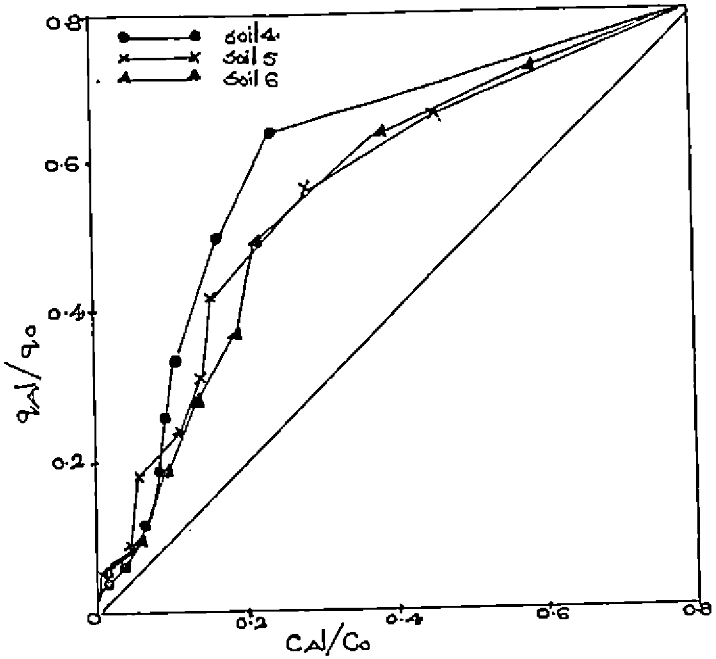

Fig.2 Normalized exchange isotherms of Al^{3+} for K^+-Al^{3+} system in laterite soils

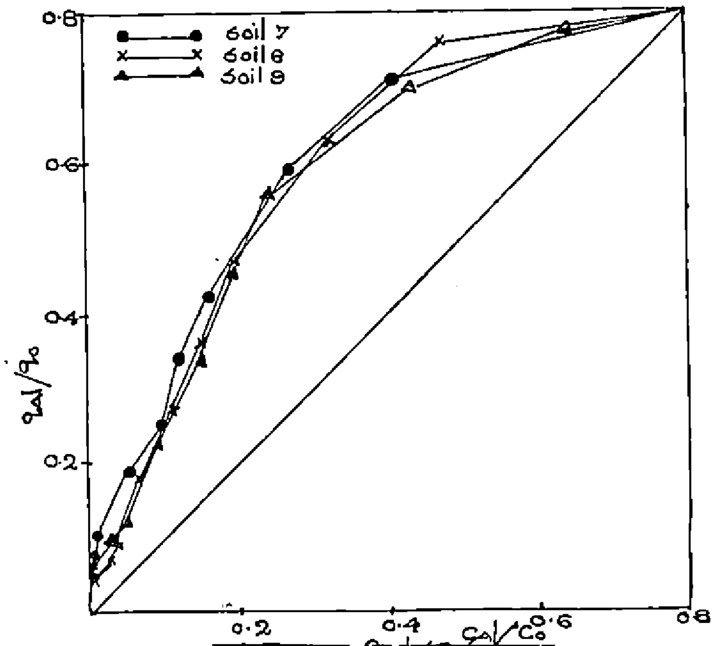

Fig.3 Normalized exchange isotherms of Al^{3+} for K^+-Al^{3+} system in redloam soils

Among the laterite soils, the maximum preference was shown by soil four, with high organic matter (Fig.2). Soil 5 with medium organic gave a slight higher preference for aluminium than soil 6, with comparatively low organic matter.

The normalized exchange isotherms for redloam soils (Fig.3) did not show much difference in their preference for aluminium to potassium.

4.1.3. Selectivity coefficients

The values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and thermodynamic equilibrium selectivity coefficient (K_N) for the three soil types are given in Tables 5, 6 and 7. In general, for all the three soil types the value of K_G increased with increase in exchangeable potassium percentage, whereas the values of other selectivity coefficients increased only upto a certain value of exchangeable potassium percentage and then decreased.

From Table 5 and Fig.4 it is clear that the values of K_G increased with increase in exchangeable potassium percentage. The increase was from 6.30 to 149.45 $\text{mol}^{-\frac{1}{3}}\ \text{l}^{\frac{1}{3}}$ for soils with high organic matter. The values of K_{KDO}, K_V and

Table 5 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) for K^+- Al^{3+} system in kari soils

Exchangeable potassium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 1		
56.82	6.30	250.57	275.90	46.64
67.13	8.19	273.06	292.22	59.39
78.39	12.54	361.55	376.76	92.02
81.86	12.88	263.34	272.39	70.17
86.87	18.19	365.43	374.19	103.85
91.13	29.66	574.99	572.57	171.51
96.11	53.17	716.40	721.18	228.07
96.42	45.84	318.98	318.64	109.29
97.68	54.76	271.49	272.56	88.07
99.53	149.45	225.94	226.11	74.89
		Soil 2		
42.57	3.66	171.72	205.49	21.46
52.03	4.41	159.60	182.32	24.94
63.02	6.86	215.70	233.35	44.16
70.84	9.01	271.21	287.57	62.21
78.61	12.37	339.14	353.23	86.56
85.05	16.08	322.83	331.61	89.92
93.86	37.81	657.13	664.14	203.63
94.41	32.25	336.41	339.70	104.94
95.94	35.22	226.52	228.10	71.97
99.21	112.34	269.36	269.72	88.96

Table 5 contd.

Exchangeable potassium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 3		
39.03	3.40	240.53	295.38	21.18
47.99	5.70	367.82	421.26	56.17
69.03	8.43	431.26	467.91	86.87
73.25	13.68	771.61	813.48	183.06
79.03	15.80	676.46	703.96	173.62
85.20	19.55	589.15	605.28	163.90
92.40	31.07	568.65	576.24	173.11
93.38	29.53	336.58	370.82	112.93
94.74	27.34	180.52	182.16	56.54
99.09	112.02	352.20	352.74	116.16

Table 6 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) for K^+- Al^{3+} system in laterite soils

Exchangeable potassium percentage	K_G ($mol^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$)	K_{KDO} (mol^{-1} l)	K_V (mol^{-1} l)	K_N (mol^{-1} l)
		Soil 4		
35.63	3.15	100.95	119.88	12.94
50.17	4.60	144.07	161.95	24.11
66.44	7.30	203.21	217.85	43.76
78.99	9.67	281.84	296.16	87.43
81.31	14.31	387.07	400.84	102.40
87.75	20.55	452.99	463.06	130.18
94.19	37.46	569.53	575.26	177.26
95.66	29.16	225.80	227.88	70.65
96.31	34.85	180.24	181.38	57.52
99.32	131.40	315.36	315.72	104.29
		Soil 5		
29.21	3.62	208.75	255.40	23.75
43.05	4.77	237.99	274.41	35.19
57.99	6.14	245.26	286.19	40.81
68.78	9.43	367.15	391.28	81.78
76.40	12.06	394.11	412.50	97.64
84.76	17.91	466.69	491.35	133.42
92.50	30.64	531.00	537.99	161.84
93.78	31.58	393.54	397.80	121.83
95.43	34.83	279.36	281.56	88.21
99.02	90.63	217.94	218.29	71.48

Table 6 contd.

Exchangeable potassium percentage	K_G (mol$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$)	K_{KDO} (mol^{-1} l)	K_V (mol^{-1} l)	K_N (mol^{-1} l)
		Soil 6		
19.82	2.96	180.86	212.78	16.81
32.11	3.62	181.57	219.11	21.89
50.53	5.45	235.99	265.03	39.68
62.98	9.38	393.77	426.02	80.56
71.84	10.76	424.20	448.71	98.69
81.23	15.20	468.09	484.83	123.69
90.44	20.01	481.17	489.36	142.93
91.40	22.91	295.60	300.09	88.89
93.51	24.35	197.33	199.56	60.84
98.59	63.01	150.26	150.75	46.72

Table 7 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) for K^+- Al^{3+} system in redloam soils

Exchangeable potassium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 7		
27.35	3.24	164.16	202.71	17.97
41.11	4.30	192.63	223.76	27.52
57.84	6.16	219.59	241.05	41.53
65.92	7.12	249.71	268.05	53.36
75.18	10.92	329.86	346.24	80.43
80.98	11.31	248.83	257.86	52.27
89.44	14.89	125.07	127.55	36.72
91.91	17.25	110.94	112.52	33.58
94.87	22.60	108.92	109.94	34.06
98.88	63.30	95.19	95.36	31.32
		Soil 8		
23.98	3.18	181.80	228.49	18.52
38.19	4.30	224.82	264.21	30.44
54.85	5.97	240.87	266.79	43.46
63.91	7.76	293.43	316.70	60.88
73.19	10.52	346.46	372.71	83.70
81.52	13.98	351.89	364.23	93.29
91.23	26.09	455.37	462.43	136.65
92.90	28.19	368.87	373.45	112.98
94.49	28.22	218.18	220.26	62.13
98.84	76.49	182.77	183.12	60.10

Table 7 contd.

Exchangeable potassium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 9		
21.96	4.51	227.08	299.73	52.75
29.78	3.79	132.92	184.16	26.79
44.35	4.56	193.69	222.25	29.31
54.24	5.84	234.01	259.69	41.80
66.52	8.56	326.55	350.01	70.40
76.52	11.39	328.73	353.98	81.87
90.00	20.35	387.18	395.25	112.26
91.02	20.55	260.39	265.16	76.76
92.28	20.99	175.45	181.90	64.52
98.37	58.46	161.27	161.71	52.86

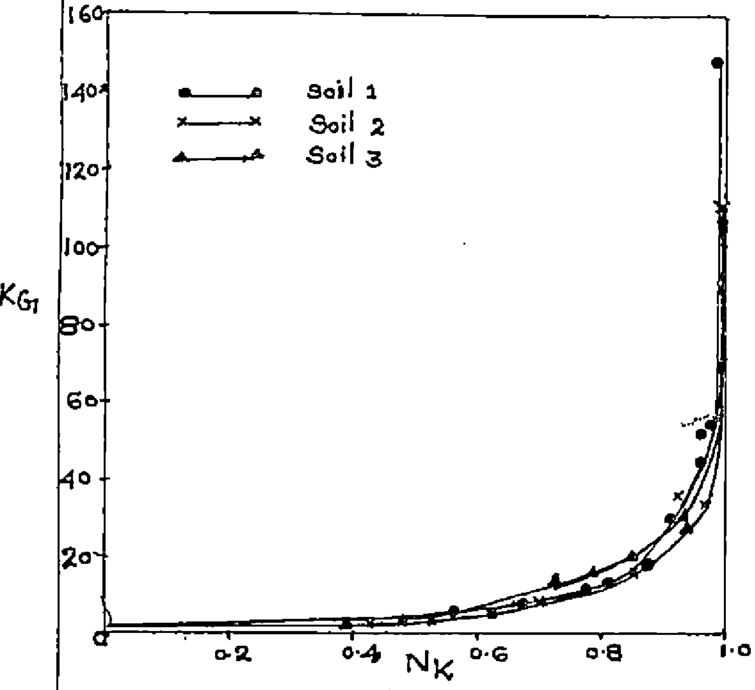

Fig. 4 Gapon selectivity coefficient (K_G) Vs. equivalent fraction of Potassium for K^+- Al^{3+} system in Kari soils

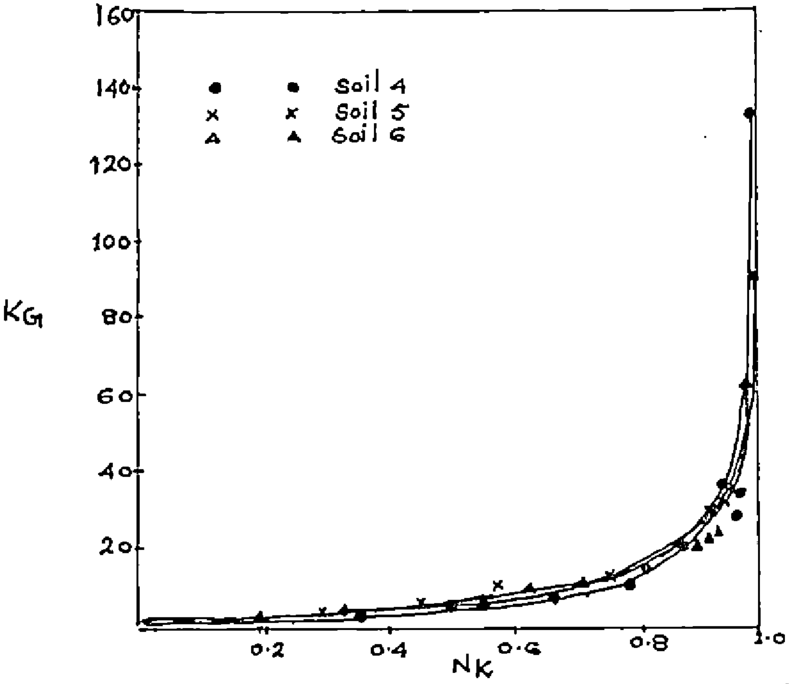

Fig. 5. Gapon selectivity coefficient vs. equivalent fraction of potassium for K^+- Al^{3+} system in lateritic soils.

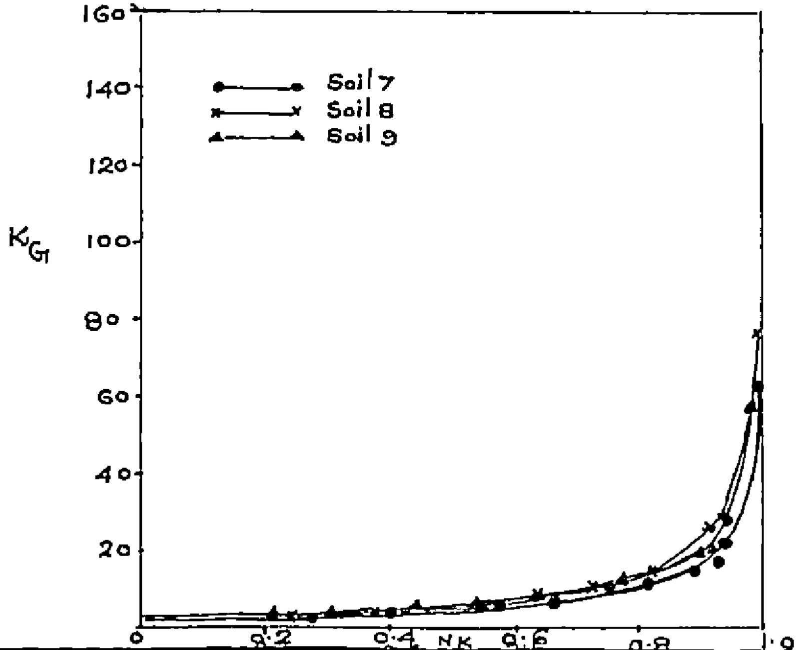

Fig. 6. Gapon Selectivity Coefficient (K_G) vs. equivalent fraction of potassium for K^+- Al^{3+} system in redloam soils

K_N increased upto an exchangeable potassium percentage of 96.11 and then decreased with further increase in exchangeable potassium percentage.

The value of K_G for soil 2 and 3 also increased with increase in exchangeable potassium percentage. For soil 2, the value of K_G increased from 3.66 to 112.34 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$, when the exchangeable potassium percentage was increased from 42.57 to 99.21. The values of K_{KDO}, K_V and K_N increased upto 93.86 percentage of potassium saturation, and then decreased. The values of all these coefficients are found to be lower than that observed for soil 1, thereby showing a decreased potassium selectivity of soil 2 compared to soil 1.

For soil 3, the value of K_G increased from 3.40 to 112.02 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$, when the exchangeable potassium percentage was increased from 39.03 to 99.09. The values of all other selectivity coefficients increased upto 73.25 percentage of potassium saturation, and then decreased.

As in the case of kari soils the values of all the selectivity coefficients for laterite soils showed the same trend (Table 6). Data on the Gapon selectivity coefficient shows an increasing potassium selectivity for all the three soils (Fig.5). When the exchangeable potassium percentage was increased from 35.63 to 99.32, the values of K_G increased from 3.15 to 131.40 mol$^{-\frac{1}{3}}$ l$^{\frac{1}{3}}$ for soil 4. The values of K_{KDO}, K_V and K_N increased upto 94.19 percentage of potassium saturation, and then decreased with further increase in potassium saturation.

For soil 5 the value of K_G increased from 3.62 to 90.63 mol$^{-\frac{1}{3}}$ l$^{\frac{1}{3}}$ when the exchangeable potassium percentage was increased from 29.21 to 99.02. For soil 6, with comparatively low organic matter, the values of K_{KDO}, K_V and K_N increased only upto 90.44 as against 92.50 and 94.19 percentage of potassium saturation for soil 5 and soil 4, respectively.

From Table 7 and Fig.6 it can be observed that the redloam soils also showed a greater preference of potassium to aluminium. Compared to the kari and laterite soils, the selectivity of redloam soils for potassium is less. For soil 7 the value of K_G increased from 3.24 to 63.30, when the exchangeable potassium percentage was increased from 27.35 to 98.88. The values of K_{KDO}, K_V and K_N increased upto 75.18 exchangeable potassium percentage. In the case of soil 8 the values of K_{KDO}, K_V and K_N increased upto 91.23 percentage of potassium saturation as against 90.00 per cent for soil 9. Generally in all the soils, there is a higher selectivity of K than Al with in the range of K-loading studied. The general shape of the K-selectivity curves are similar for all the soils.

4.1.4. Correlation studies

Coefficients of correlations (r) between exchangeable potassium percentage and various selectivity coefficients are given in Table 8. Among the various selectivity coefficients the values of r, in general, were maximum for K_N, followed by K_V, K_{KDO}, and K_G. K_G was found to be least dependent on exchangeable potassium percentage. Among the kari soils the value of r for K_G and K_N were maximum for soil 2 with medium organic matter, followed by soil 3 and soil 1. The value of 'r' for K_{KDO} is 0.5032, 0.5711 and 0.7235 for soils 1, 2 and 3 respectively. The correlation coefficient (r) for K_V is found to be maximum for soil 3 followed by soil 1 and soil 2.

As in the case of kari soils the dependence of various selectivity coefficients, on exchangeable potassium percentage followed the order $K_N > K_V > K_{KDO} > K_G$. Among the laterite soils, soil 4 with high organic matter showed the maximum correlation between exchangeable potassium percentage and various selectivity coefficients than soil 5 and 6 with

Table 8 Values of correlation coefficient (r) for exchangeable potassium percentage versus exchange selectivity coefficients in $K^+ - Al^{3+}$ system

Soil	K_G	K_{KDO}	K_V	K_N
1	0.5226	0.5032	0.9225**	0.8833**
2	0.8029**	0.5711	0.8477**	0.9825**
3	0.5388	0.7235*	0.9476**	0.9550**
4	0.5725	0.5921	0.9385**	0.9848**
5	0.5729	0.5622	0.7092*	0.9654**
6	0.3274	0.3157	0.6154	0.9808**
7	0.5192	0.9021**	0.9560**	0.9768**
8	0.6172	0.5773	0.6921*	0.9630**
9	0.7402*	0.4376	0.7478*	0.9523**

* Significant at 5% level

** Significant at 1% level

medium and low organic matter. The values of r for K_G, K_{KDO}, K_V and K_N are 0.5725, 0.5921, 0.9385 and 0.9848 for soil 4 as against 0.5729, 0.5622, 0.7092, 0.9654 for soil 5 and 0.3274, 0.3157, 0.6154 and 0.9808 for soil 6.

As in the case of laterite soils among the redloam soils, soil 7 with high organic matter showed the maximum correlation between exchangeable potassium percentage and various selectivity coefficients. Thermodynamic equilibrium selectivity coefficient (K_N) was found to be highly dependent on exchangeable potassium percentage. Gapon selectivity coefficient was found to be least dependent on exchangeable potassium percentage. The value of 'r' for K_N is 0.9768 as against 0.5192 for K_G in the case of soil 7.

4.1.5. Free energy change

The weighted mean values of the approximate free energy change ($\triangle G^\circ$) for the exchange reaction : Al-soil + $3K^+ \rightleftharpoons 3K$- soil + Al^{3+}, for the whole exchange isotherm for kari, laterite and redloam soils are given in Table 9. The negative values of $\triangle G^\circ$ suggested that the reaction was spontaneous, showing higher preference of K to Al.

Among the kari soils, the value of $\triangle G^\circ$ was minimum

Table 9 Calculated values of standard free energy change (ΔG°, Cal eq^{-1}) of K^+- Al^{3+} exchange in relation to organic matter content for kari, laterite and redloam soils

Soil type	Organic matter content		
	High	Medium	Low
Kari	-2303	-2523	-2780
Laterite	-2636	-2832	-2856
Redloam	-2796	-2939	-2965

for soil 1 with high organic matter. For soil 1 the value of $\triangle G^\circ$ was $^-2303$ cal eq^{-1} as against $^-2523$ and $^-2780$ cal eq^{-1} for soil 2 and 3, with medium and low organic matter. The same trend was observed for laterite and redloam soils. Comparing soils on the basis of $\triangle G^\circ$, the preference was in the order redloam soils > laterite soils > kari soils.

4.2. Aluminium-Calcium system

4.2.1. Effect of different electrolyte concentration and organic matter on aluminium-calcium exchange

Tables 10, 11 and 12 present the data on the equilibrium concentrations of aluminium and calcium in kari, laterite and redloam soils, respectively. As in the case of potassium-aluminium system, here also with increase in the equivalent fraction of aluminium in the equilibriating solution, more of aluminium was adsorbed into the soil solid and corresponding amount of calcium was desorbed into the soil solution in all the three soil types. Compared to the potassium-aluminium system the amount of aluminium adsorption was less in calcium-aluminium system.

Among the kari soils, soil 1 with high organic matter adsorbed more aluminium than soil 2 and soil 3 with medium and low organic matters. At an equivalent fraction of 1.00

Table 10 Equilibrium concentration of aluminium (Al) and calcium (Ca) for Ca^{2+}- Al^{3+} system in kari soils

Sl. No.	Soil 1				Soil 2				Soil 3			
	q_{Al} (Cmol (+) kg^{-1}	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1}	CCa (me l^{-1})
1	0.18	0.02	37.82	19.98	0.16	0.04	20.04	19.96	0.14	0.06	15.26	19.94
2	0.87	0.13	37.13	19.87	0.71	0.29	19.49	19.71	0.52	0.48	14.88	19.52
3	1.24	0.26	36.76	19.74	0.98	0.52	19.22	19.48	0.77	0.73	14.63	19.27
4	1.52	0.48	36.48	19.52	1.20	0.80	19.00	19.20	1.06	0.94	14.34	19.06
5	3.13	0.87	34.87	19.13	2.23	1.77	19.97	18.23	2.12	1.88	13.28	18.12
6	4.51	1.49	33.49	18.51	3.44	2.56	16.76	17.44	3.15	2.85	12.25	17.15
7	6.07	1.93	31.93	18.07	4.70	3.30	15.50	16.70	4.33	3.67	11.07	16.33
8	7.60	2.40	30.40	17.60	6.26	3.74	13.74	16.26	5.37	4.63	10.03	15.37
9	11.50	3.50	26.50	16.50	8.69	6.31	11.51	13.69	7.96	7.04	7.44	12.96
10	14.30	5.70	23.70	14.30	11.31	8.69	8.89	11.31	9.55	10.45	5.85	9.55

q - adsorbed phase

C - solution phase

Table 11 Equilibrium concentration of aluminium (Al) and calcium (Ca) for Ca^{2+}- Al^{3+} system in laterite soil

Sl. No.	Soil 4				Soil 5				Soil 6			
	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})
1	0.16	0.04	23.44	19.96	0.15	0.05	16.25	19.95	0.14	0.06	11.26	19.94
2	0.76	0.24	22.84	19.76	0.74	0.26	15.66	19.74	0.67	0.33	10.73	19.67
3	1.02	0.48	22.58	19.52	0.96	0.54	15.44	19.46	0.91	0.59	10.49	19.41
4	1.23	0.77	22.37	19.23	1.04	0.96	15.36	19.04	1.08	0.92	10.32	19.08
5	2.72	1.28	20.88	18.72	2.16	1.84	14.24	18.16	2.06	1.94	9.34	18.06
6	4.10	1.90	19.50	18.10	3.29	2.71	13.11	17.29	3.06	2.94	8.34	17.06
7	5.38	2.62	18.22	17.38	4.37	3.63	12.03	16.37	3.89	4.11	7.51	15.89
8	6.84	3.16	16.76	16.84	5.71	4.29	10.69	15.71	5.21	4.79	6.19	15.21
9	10.13	4.87	13.47	15.13	8.18	6.82	8.22	13.18	6.67	8.33	4.73	11.67
10	13.58	6.42	10.02	13.58	10.53	9.47	5.87	10.53	8.22	11.78	3.18	8.22

q - adsorbed phase

C - solution phase

Table 12 Equilibrium concentration of aluminium (Al) and calcium (Ca) for Ca^{2+}- Al^{3+} system in redloam soil

Sl. No.	Soil 7				Soil 8				Soil 9			
	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Ca} (Cmol (+) kg^{-1})	CCa (me l^{-1})
1	0.15	0.05	16.05	19.95	0.14	0.06	13.66	19.94	0.11	0.09	9.09	19.91
2	0.74	0.26	15.46	19.74	0.64	0.36	13.16	19.64	0.68	0.32	8.52	19.68
3	0.98	0.52	15.22	19.48	0.94	0.56	12.86	19.44	0.91	0.59	8.29	19.41
4	1.23	0.77	14.97	19.23	1.16	0.84	12.64	19.16	1.02	0.98	8.18	19.02
5	2.53	1.47	13.67	18.53	2.13	1.87	11.67	18.13	2.24	1.76	6.96	18.24
6	3.77	2.23	12.43	17.77	3.17	2.83	10.63	17.17	3.06	2.94	6.14	17.06
7	5.04	2.96	11.16	17.04	4.18	3.82	9.62	16.18	4.00	4.00	5.20	16.00
8	6.46	3.54	9.74	16.46	5.15	4.85	8.65	15.15	4.62	5.38	4.58	14.62
9	9.07	5.93	7.13	14.07	7.73	7.27	6.07	12.73	6.43	3.57	2.77	11.43
10	11.02	8.98	5.18	11.02	9.46	10.54	4.34	9.46	7.08	12.92	2.12	7.08

q - adsorbed phase

C - solution phase

aluminium the amount of aluminium adsorbed by soil 1 was 14.30 as against 11.31 and 9.55 Cmol (+) kg^{-1} by soil 2 and 3, respectively.

The same trend was observed in laterite soils also. Compared to the kari soils the amount of aluminium adsorbed by these soils was less. When the equivalent fraction of aluminium in the equilibriating solution was increased from 0.01 to 1.00, the quantity of aluminium adsorbed by soil 4 increased from 0.16 to 13.58 Cmol (+) kg^{-1}. For soil 5 the increase was from 0.15 to 10.53 Cmol (+) kg^{-1} as against the increase from 0.14 to 8.22 Cmol (+) kg^{-1} for soil 6.

From Table 12 it is clear that the amount of aluminium adsorbed by redloam soils was less than that observed in kari and laterite soils. The quantity of aluminium adsorbed by soil 7 was 11.02 Cmol (+) kg^{-1} as against 9.46 and 7.08 Cmol (+) kg^{-1} by soil 8 and soil 9, respectively, when these soils were equilibriated with an electrolyte containing the maximum equivalent fractions of aluminium (1.00).

4.2.2. Exchange isotherms

The normalized exchange isotherms of aluminium for kari soils (Fig. 7) lay above the diagonal, showing the

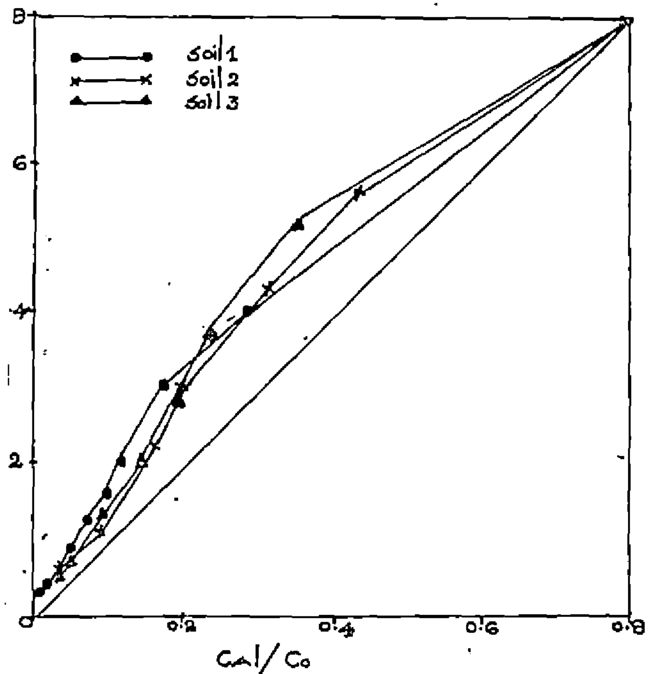

Fig.7 Normalized exchange isotherms of Al for Ca^{2+}-Al^{3+} system in kari soils

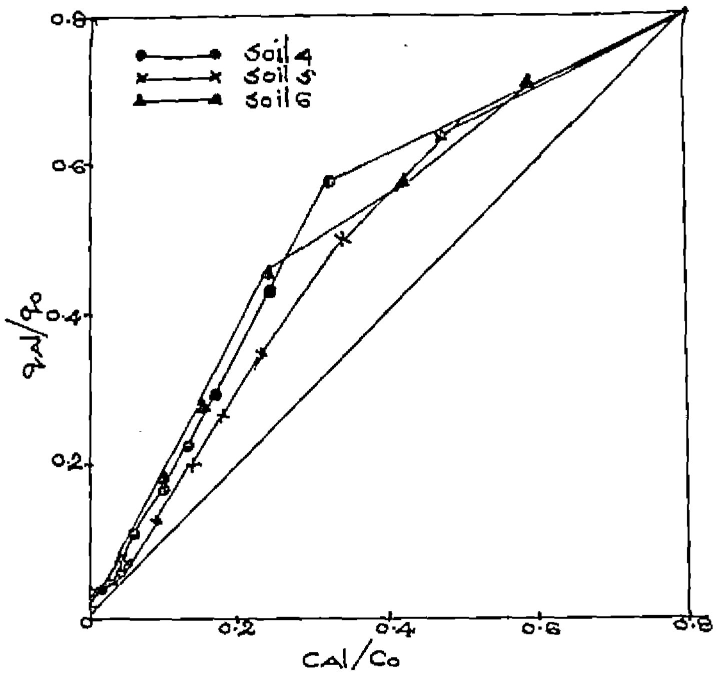

Fig.8 Normalized exchange isotherms of Al^{3+} for Ca^{2+}-Al^{3+} system in laterite soils

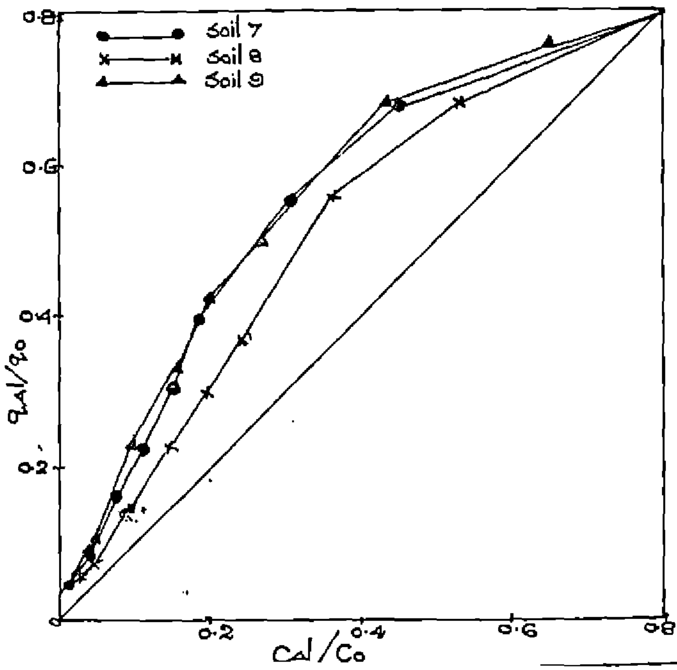

Fig.9 Normalized exchange isotherms of Al^{3+} for Ca^{2+}-Al^{3+} system in redloam soils

preferential adsorption of aluminium to calcium by all the three soils. Soil 1 showed the maximum preference compared to soil 2 and 3.

As in the case of kari soils, for laterite soils also the isotherms lay above the diagonal (Fig.8). Here the preference followed the order soil 4 > soil 6 > soil 5.

Fig.9 shows the normalized exchange isotherms of aluminium for redloam soils. The isotherms lay above the diagonal, suggesting higher preference in all the three soils for aluminium to calcium. Soils 7 and 9 show only marginal difference in their preference for aluminium. Soil 8 shows the minimum preference for aluminium.

4.2.3. Selectivity coefficients

Table 13 presents the data on the calculated values of K_G, K_{KDO}, K_V and K_N for kari soils. Similar to the potassium-aluminium system the values of K_G increased with increase in calcium saturation. The calcium selectivity curve (Fig.10) for the three soils showed an increasing calcium selectivity with increasing exchangeable calcium percentage. At 62.39 per cent calcium saturation the value of K_G was 2.04 mol$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$, and it increased to 33.51 mol$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ when the exchangeable calcium percentage was increased to

Table 13 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) for Ca^{2+}- Al^{3+} system in kari soils

Exchangeable calcium percentage	K_G ($mol^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$)	K_{KDO} (mol^{-1} l)	K_V (mol^{-1} l)	K_N (mol^{-1} l)
		Soil 1		
62.39	2.04	13.53	15.47	6.01
69.74	2.54	7.28	8.10	3.24
80.00	3.44	9.83	10.52	4.37
84.03	4.04	10.70	11.30	4.75
88.13	5.17	12.44	12.95	5.53
91.76	7.13	9.04	9.29	5.82
96.00	11.16	8.61	8.78	5.60
96.74	11.18	5.51	5.57	2.45
97.71	12.74	2.83	2.85	1.26
99.53	33.51	1.63	1.63	0.72
		Soil 2		
44.01	1.25	9.91	12.18	4.41
56.98	1.72	10.99	12.83	4.89
70.39	2.47	7.76	8.66	5.04
76.73	3.14	14.10	15.28	6.27
82.97	4.18	17.66	18.73	7.85
88.96	5.98	27.21	28.15	9.69
94.06	8.80	15.97	15.66	9.60
95.15	9.38	9.85	10.01	4.38
96.48	10.74	5.89	5.96	2.62
99.21	25.18	2.31	2.32	1.03

Table 13 contd.

Exchangeable calcium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 3		
37.98	1.13	12.34	15.56	5.48
48.31	1.30	6.78	8.19	3.01
65.13	2.07	9.61	10.87	3.75
71.88	2.55	10.48	11.59	4.65
79.54	3.49	14.04	15.07	6.24
86.23	4.76	14.65	15.36	6.87
93.12	7.97	15.96	16.33	7.10
95.00	10.23	18.77	19.08	8.34
96.62	13.31	18.05	18.25	8.31
99.09	27.53	3.94	3.96	3.07

Table 14 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficients (K_V), equilibrium selectivity coefficients (K_N) for Ca^{2+}- Al^{3+} system in laterite soils

Exchangeable calcium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 4		
42.46	0.97	2.70	3.34	1.23
57.08	1.51	4.95	5.77	2.19
71.02	2.29	6.44	7.13	2.86
77.21	2.93	8.40	9.09	3.74
82.63	3.63	8.30	8.81	3.69
88.47	5.05	9.54	9.92	4.23
94.79	9.98	19.16	19.49	8.53
95.68	10.30	10.69	10.84	4.75
96.78	11.03	3.23	4.86	2.14
99.32	29.45	3.16	3.17	1.41
		Soil 5		
35.79	0.94	5.94	7.55	2.64
50.12	1.37	7.26	8.11	3.23
65.18	2.01	7.88	8.80	3.46
73.38	2.73	12.05	13.22	5.35
79.94	3.50	20.81	22.30	5.81
86.83	4.97	15.57	16.29	6.91
93.66	6.76	20.01	20.44	8.89
94.15	7.79	7.19	7.33	3.15
95.49	7.98	2.78	2.82	1.23
99.08	23.33	2.70	2.71	1.19

Table 14 contd.

Exchangeable calcium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 6		
27.89	0.79	7.28	9.57	3.17
41.49	1.09	5.96	7.39	2.83
54.35	1.34	3.59	4.23	1.89
66.94	2.03	7.43	8.38	3.30
73.22	2.48	6.85	7.52	3.04
82.00	3.49	7.84	8.34	3.49
90.61	5.58	7.39	7.64	3.29
92.10	5.76	3.62	4.39	1.90
94.12	6.55	2.55	2.60	1.13
98.86	18.52	2.14	2.15	0.95

Table 15 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) for Ca^{2+} - Al^{3+} system in redloam soils

Exchangeable calcium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 7		
31.75	0.76	2.97	3.84	1.29
44.01	0.99	2.44	2.38	1.08
60.12	1.48	2.77	3.19	1.23
68.89	2.02	4.33	4.83	1.93
76.73	2.68	5.38	5.85	2.39
84.38	3.74	7.46	7.87	2.72
92.41	6.67	8.39	8.61	3.73
93.95	7.43	6.10	6.23	2.71
95.43	7.88	2.70	2.74	1.20
99.07	23.17	2.64	2.64	1.17
		Soil 8		
31.45	0.85	6.50	7.77	2.66
43.98	1.11	3.67	3.77	2.17
62.68	1.91	8.56	9.77	3.80
69.11	2.34	9.16	10.19	4.07
77.03	2.30	17.11	18.53	4.41
84.56	4.15	10.86	11.45	4.82
91.59	6.16	8.03	8.26	3.55
93.19	6.71	6.32	6.46	2.43
95.36	8.66	4.43	4.50	2.26
98.98	22.56	3.16	3.17	1.42

Table 15 contd.

Exchangeable calcium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 9		
23.04	0.68	6.61	8.89	2.94
30.11	0.68	1.92	2.50	0.85
49.78	1.19	3.23	3.88	1.44
56.52	1.55	2.68	3.14	1.19
66.74	1.82	3.39	3.81	1.51
75.65	2.30	2.72	2.96	1.21
88.91	4.79	5.86	6.09	2.60
90.11	4.55	2.22	2.29	1.16
92.61	5.07	1.44	1.48	0.64
98.80	21.79	5.11	5.13	2.27

99.53. The values of K_{KDO}, K_V and K_N increased upto 88.13 per cent of calcium saturation and then decreased with further increase in exchangeable calcium percentage. For soil 2 and 3 also a similar trend was observed. The value of K_{KDO}, K_V and K_N for soil 2 and 3 increased upto 88.96 and 95.00 per cent of calcium saturation, respectively.

The calculated values of K_G, K_{KDO}, K_V and K_N for laterite soils are given in Table 14. The Gapon selectivity coefficient data as depicted in Fig.11 suggests a higher selectivity of calcium than aluminium. However, the values of all the selectivity coefficients were lower than that obtained for kari soils, thereby showing a relatively lower selectivity of laterite soils for calcium compared to kari soils.

For soil 4 the value of K_G increased from 0.97 to 29.45 $mol^{-\frac{1}{2}}\ 1^{\frac{1}{2}}$ when the exchangeable calcium percentage was increased from 42.46 to 99.32. In the case of soil 5 the increase in K_G was from 0.94 to 23.33 and $mol^{-\frac{1}{2}}\ 1^{\frac{1}{2}}$ as a result of the increase in exchangeable calcium percentage from 35.79 to 99.08. As in the case of kari soils the values of K_{KDO}, K_V and K_N for soil 4 end 5 increased upto a certain value of exchangeable calcium percentage and then decreased, with further increase in calcium saturation. The value of

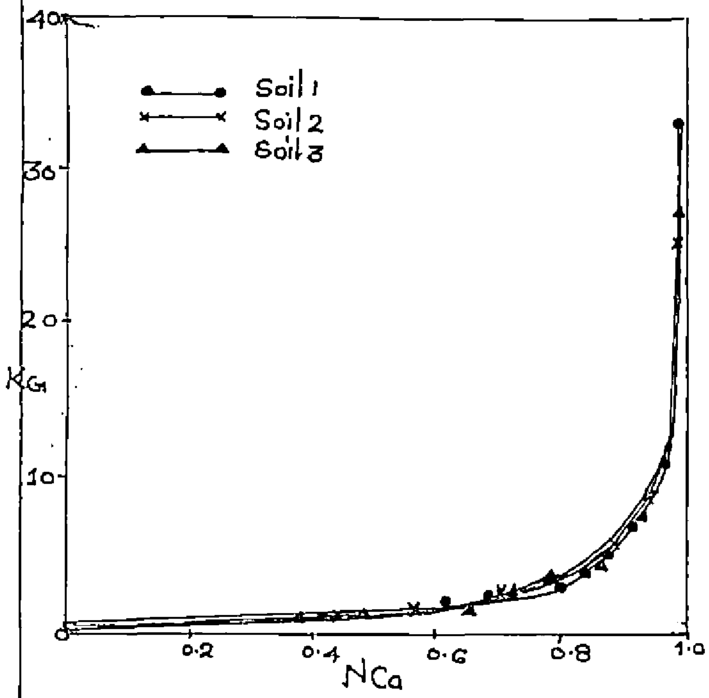

Fig. 10. Gapon Selectivity coefficient (K_G) vs. equivalent fraction of calcium (N ca) for Ca^{2+}-Al^{3+} system in kari soils.

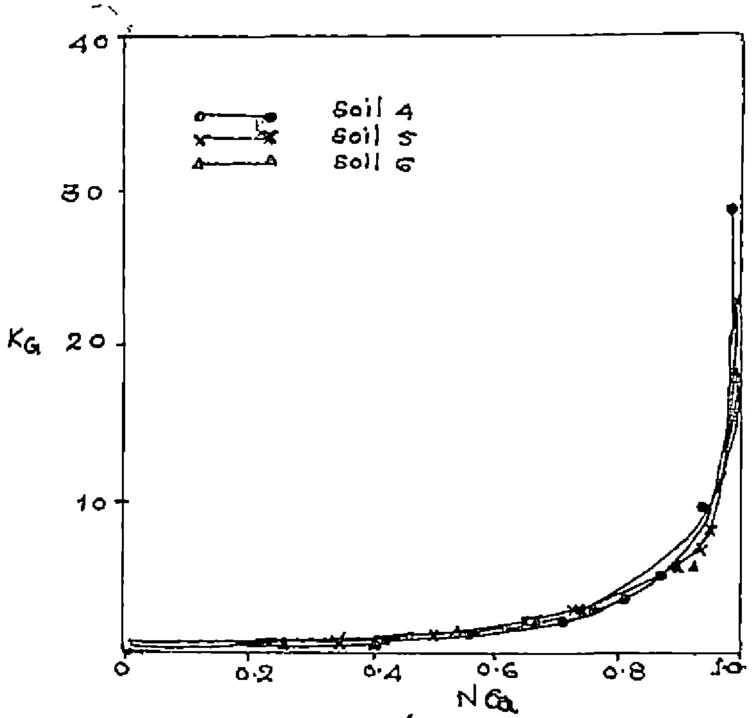

Fig. 11 Gapon Selectivity Coefficient (K_G) vs. equivalent fraction of calcium (N Ca) for Ca^{2+}-Al^{3+} system in laterite soils

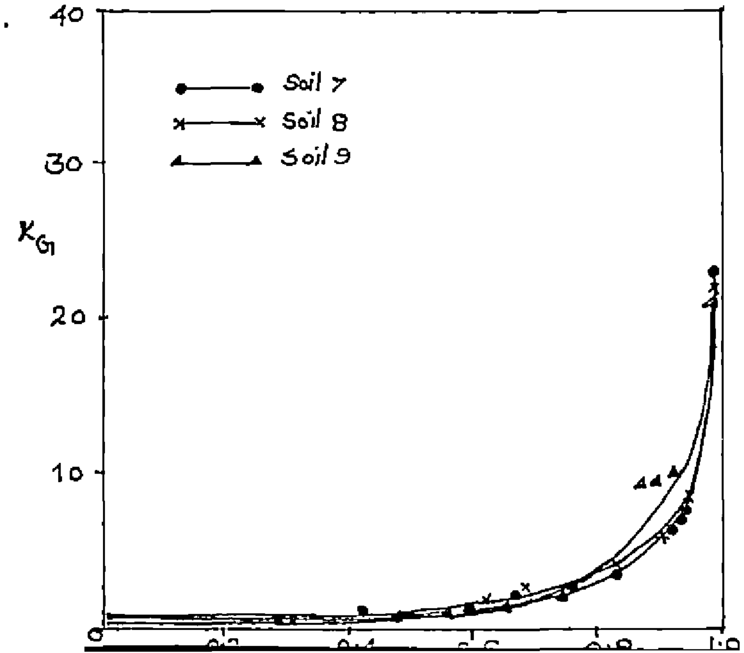

Fig 12 Gapon selectivity coefficient (K_G) vs. equivalent fraction of calcium (N Ca) for Ca^{2+}-Al^{3+} system in redloam soils.

K_G for soil 6 also showed the same trend but the values of the remaining selectivity coefficients vary irregularly with change in exchangeable calcium percentage.

For redloam soils, the data presented in Table 15 suggests that they also showed the same trend as observed in kari and laterite soils. The value of K_G for soil 7 increased from 0.76 to 23.17 $mol^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ when the exchange calcium percentage was increased from 31.75 to 99.07. Soil 8 with comparatively medium organic matter showed an increase in K_G value from 0.85 to 22.56 $mol^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$, as a result of the increase in exchangeable calcium percentage from 31.45 to 98.98. The value of K_{KDO}, K_V and K_N increased upto 92.41 and 77.03 per cent calcium saturation for soil 7 and soil 8 respectively. The values were found to be lower than that obtained for laterite soils.

For soil 9 with low organic matter gave K_G value lower than that obtained for soil 7 and 8. The trend was same as in the previous cases. In this soil the values of K_{KDO}, K_V and K_N remained more or less constant, except for a few values.

4.2.4. Correlation studies

From Table 16 it is clear that the coefficients of

Table 16 Values of correlation coefficient (r) for exchangeable calcium percentage versus exchange selectivity coefficients in Ca^{2+}- Al^{3+} system

Soil	K_G	K_{KDO}	K_V	K_N
1	0.9513^{**}	0.9677^{**}	0.9794^{**}	0.9897^{**}
2	0.8409^{**}	0.9423^{**}	0.9740^{**}	0.9894^{**}
3	0.9005^{**}	0.9294^{**}	0.9541^{**}	0.9673^{**}
4	0.9281^{**}	0.9747^{**}	0.9766^{**}	0.9868^{**}
5	0.8788^{**}	0.9620^{**}	0.9742^{**}	0.9885^{**}
6	0.9149^{**}	0.9587^{**}	0.9663^{**}	0.9738^{**}
7	0.9317^{**}	0.9533^{**}	0.9835^{**}	0.9911^{**}
8	0.9220^{**}	0.9487^{**}	0.9849^{**}	0.9885^{**}
9	0.9202^{**}	0.9444^{**}	0.9844^{**}	0.9889^{**}

* Significant at 5% level

** Significant at 1% level

correlations for all the selectivity coefficients were higher than that obtained for potassium-aluminium system. As in the case of potassium-aluminium system the values of r were maximum for K_N and minimum for K_G in this system also. The value of r for K_N is 0.9897 as against 0.9513 for K_G. The values of r, in general, followed the trend $K_N > K_V > K_{KDO} > K_G$. Among the three soils the dependence of selectivity coefficients on exchangeable calcium percentage, in general, followed the trend soil 1 > soil 2 > soil 3.

For laterite soils the same trend was observed (Table 16). Soil 4 with comparatively high organic matter showed the maximum correlation between exchangeable calcium percentage and various selectivity coefficients, followed by soil 5 and 6 with medium and low organic matter. For the various selectivity coefficients the value of r, in general, followed the trend $K_N > K_V > K_{KDO} > K_G$. For soil 4 the value of r for K_N is 0.9868 as against 0.9766 for K_V, 0.9747 for K_{KDO} and 0.9281 for K_G.

As in the above two soil types, redloam soils also showed a high correlation between exchangeable calcium percentage and various selectivity coefficients. Soil 7 with relatively high organic matter showed the maximum correlation between the two. The value of r for K_N is 0.9911 for soil 7 as against 0.9885 for soil 8, and 0.9889 for soil 9. Among the soils the dependence followed the order soil 7 > soil 8> soil 9. For the various selectivity coefficients the dependence followed the same trend as observed in kari and laterite soils.

4.2.5. Free energy change

The weighted mean value's of the approximate free energy change ($\triangle G^{\circ}$) for the exchange reaction 2 Al-soil + $3\ Ca^{2+} \rightleftharpoons 3\ Ca\text{-}Soil + 2\ Al^{3+}$, for the whole exchange isotherms are given in Table 17. As in the case of K-Al exchange, here also the values were negative, indicating preference for Ca^{2+} to Al^{3+}. However, the values were smaller than that obtained for K-Al exchange. For soil 1, 2 and 3, with high, medium and low organic matter, the values of $\triangle G^{\circ}$ were -905, -1049 and -1131 Cal eq^{-1}, respectively. The same trend was observed for laterite soils. Among the redloam soils the value of $\triangle G^{\circ}$ was maximum for soil 8 (-961 Cal eq^{-1}) with medium organic matter and minimum for soil 9 (-723 Cal eq^{-1}) with low organic matter.

4,3. Aluminium-magnesium system

4.3.1. Effect of different electrolyte concentrations and organic matter on aluminium-magnesium exchange

From Table 18 it is clear that exchange of aluminium

Table 17 Calculated values of standard free energy change (ΔG°, Cal eq^{-1}) of Ca^{2+}- Al^{3+} exchange in relation to organic matter content for kari, laterite and redloam soils

Soil type	Organic matter content		
	High	Medium	Low
Kari	-905	-1049	-1131
Laterite	-936	-975	-984
Redloam	-792	-961	-723

Table 18 Equilibrium concentration of aluminium (Al) and magnesium (mg) for Mg^{2+}- Al^{3+} system in kari soils

Sl. No.	Soil 1				Soil 2				Soil 3			
	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})
1	0.17	0.03	37.83	19.97	0.16	0.04	20.04	19.96	0.09	0.11	15.31	19.89
2	0.81	0.19	37.19	19.81	0.71	0.29	19.49	19.71	0.41	0.59	14.99	19.41
3	1.19	0.31	36.81	19.69	0.99	0.51	19.21	19.49	0.61	0.89	14.79	19.11
4	1.38	0.62	36.62	19.38	1.18	0.82	19.02	19.18	0.74	1.26	14.66	18.74
5	2.79	1.21	35.21	18.79	2.16	1.84	18.04	18.86	1.68	2.32	13.72	17.68
6	4.24	1.76	33.76	18.24	3.41	2.59	16.79	17.41	2.62	3.38	12.78	16.62
7	5.76	2.24	32.24	17.76	4.68	3.32	15.52	16.68	3.58	4.42	11.82	15.58
8	7.26	2.74	30.74	17.26	6.04	3.96	14.16	16.04	4.52	5.48	10.88	14.52
9	10.92	4.08	27.08	15.92	8.67	6.33	11.53	13.67	6.72	8.28	8.68	11.72
10	13.97	6.03	24.03	13.97	11.32	8.68	8.88	11.32	9.52	10.48	5.88	9.52

q - adsorbed phase

C - solution phase

Table 19 Equilibrium concentration of aluminium (Al) and magnesium (mg) for Mg^{2+}- Al^{3+} system in laterite soils

Sl. No.	Soil 4				Soil 5				Soil 6			
	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})
1	0.17	0.03	23.43	19.97	0.14	0.06	16.26	19.94	0.13	0.07	11.27	19.93
2	0.76	0.24	22.84	19.76	0.75	0.25	15.65	19.75	0.67	0.33	10.73	19.67
3	0.98	0.52	22.62	19.48	0.97	0.53	15.43	19.47	0.93	0.57	10.47	19.43
4	1.26	0.74	22.34	19.26	1.05	0.95	15.35	19.05	1.02	0.98	10.38	19.02
5	2.73	1.27	20.87	18.73	2.07	1.93	14.33	18.07	2.13	1.87	9.27	18.13
6	4.12	1.88	19.48	18.12	3.18	2.82	13.22	17.18	3.02	2.98	8.38	17.02
7	5.47	2.53	18.13	17.47	4.19	3.81	12.21	16.19	3.77	4.23	7.63	15.77
8	6.82	3.18	16.78	16.82	5.24	4.76	11.16	15.24	5.09	4.91	6.31	15.09
9	10.07	4.93	13.53	15.07	7.67	7.33	8.73	12.67	6.73	8.27	4.76	11.73
10	13.12	6.88	10.48	13.12	9.97	10.03	6.43	9.97	7.87	12.13	3.53	7.87

q - adsorbed phase

C - solution phase

Table 20 Equilibrium concentration of aluminium (Al) and magnesium (mg) for Mg^{2+} - Al^{3+} system in redloam soils

Sl. No.	Soil 7				Soil 8				Soil 9			
	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{MG} (Cmol (+) kg^{-1})	CMg (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})	q_{Al} (Cmol (+) kg^{-1})	CAl (me l^{-1})	q_{Mg} (Cmol (+) kg^{-1})	CMg (me l^{-1})
1	0.16	0.04	16.04	19.96	0.15	0.05	13.65	19.95	0.13	0.07	9.07	19.93
2	0.76	0.28	15.44	19.72	0.72	0.28	13.08	19.72	0.65	0.34	8.54	19.66
3	1.02	0.48	15.18	19.52	1.06	0.44	12.74	19.56	1.01	0.49	8.19	19.51
4	1.32	0.68	14.88	19.32	1.26	0.74	12.54	19.26	1.23	0.77	7.97	19.23
5	2.48	1.52	13.72	18.48	2.14	1.86	11.66	18.14	2.14	1.86	7.06	18.14
6	3.69	2.31	12.51	17.69	3.13	2.87	10.67	17.13	3.02	2.98	6.18	17.02
7	5.06	2.94	11.18	17.02	4.11	3.89	9.69	16.11	4.02	3.98	5.18	16.02
8	6.23	3.77	9.97	16.23	5.18	4.82	8.62	15.18	5.14	4.86	4.06	15.14
9	8.97	6.03	7.23	13.97	7.03	7.97	6.77	12.03	6.13	8.87	3.07	11.13
10	10.42	9.58	5.78	10.42	9.14	10.86	4.66	9.14	7.06	12.94	2.14	7.06

q - adsorbed phase

C - solution phase

for magnesium increases with increase in the concentration of aluminium in the equilibriating solution. Compared to the other two systems the exchange was less.

Among the kari soils, soil 1 with relatively high organic matter exchanged more aluminium compared to soil 2 and 3. For soil 1 the value of exchangeable aluminium was 13.97 Cmol (+) kg^{-1} as against 11.32 and 9.52 Cmol (+) kg^{-1} for soil 2 and 3, respectively, when these soils were equilibriated with a solution containing 1.00 equivalent fraction of aluminium.

Compared to kari soils, laterite soils exchanged lower amount of aluminium for magnesium (Table 19). For soil 4, when the equivalent fraction of aluminium in the equilibriating solution was increased from 0.01 to 1.00, the exchangeable aluminium increased from 0.17 to 13.12 Cmol (+) kg^{-1}. For soil 5 the increase was from 0.14 to 9.97 Cmol (+) kg^{-1}, soil 6 gave still lower values (from 0.13 to 7.87). This suggests a decreasing aluminium adsorbing tendency with decreasing organic matter.

Table 20 presents the data on the equilibrium concentrations of aluminium and magnesium for redloam soils. These soils also showed the same trend as observed in laterite and kari soils. Compared to the other types of soils, these soils adsorbed less amount of aluminium for each successive increase in the aluminium concentration in the electrolyte. Among the redloam soils, soil 7 with comparatively high organic matter adsorbed 10.42 Cmol (+) kg^{-1} of aluminium as against 9.14 and 7.06 Cmol (+) kg^{-1} for soil 8 and 9, with medium and low organic matter, respectively, when all the three soils are equilibriated with a solution containing 1.00 equivalent fraction of aluminium.

4.3.2. Exchange isotherms

Figure 13 shows the normalized exchange isotherms of aluminium for kari soils. As in the case of potassium-aluminium and calcium-aluminium system, the isotherms lay above the diagonal, suggesting higher preference in all the soils for aluminium to magnesium. Here the preference, in general followed the order: soil 2 > soil 1 > soil 3.

The normalized exchange isotherms of aluminium for laterite soils also lay above the diagonal, indicating a preferential adsorption of aluminium to calcium (Fig.14). Soils 7 and 9 showed almost the same preference for aluminium. Soil 8 showed the minimum preference.

For redloam soils, the normalized exchange isotherm,

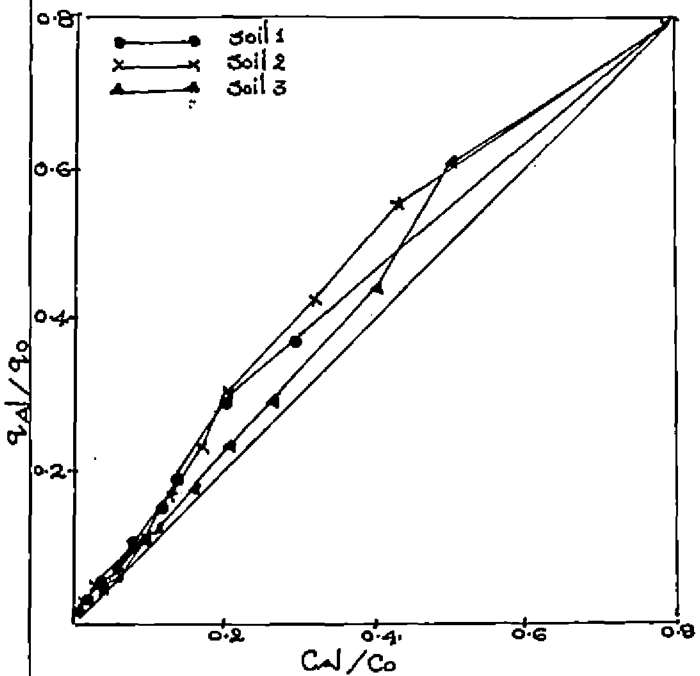

Fig.13 Normalized exchange isotherms of Al^{3+} for Mg^{2+}-Al^{3+} system in kari soils.

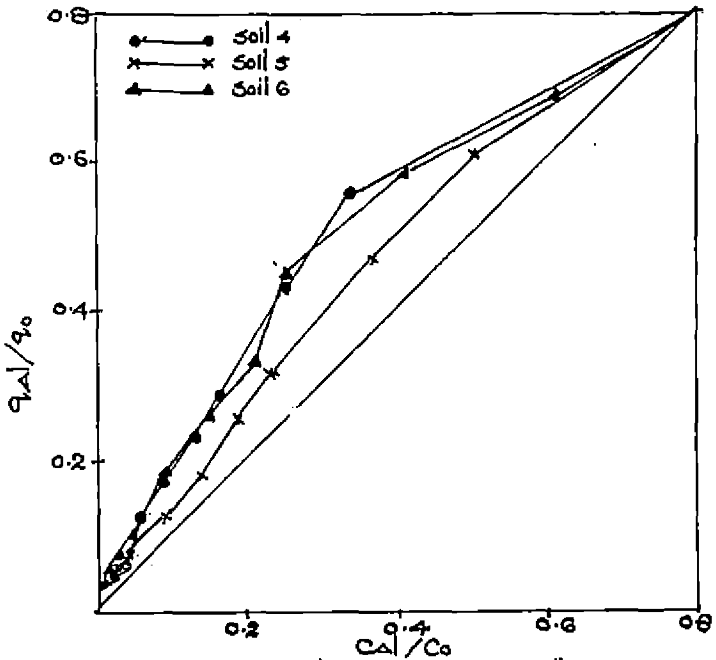

Fig.14 Normalized exchange isotherms of Al^{3+} for Mg^{2+}-Al^{3+} system in laterite soils

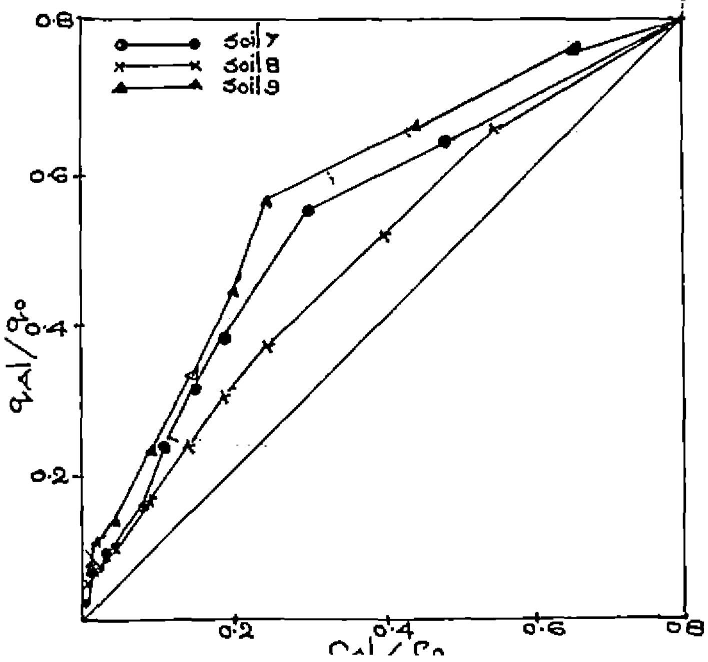

Fig.15 Normalized exchange isotherms of Al^{3+} for Mg^{2+}-Al^{3+} system in redloam soils

as depicted in Fig.15 suggest a higher preference for aluminium to magnesium. Here the preference followed the order: soil 9 > soil 7 > soil 8.

4.3.3. Selectivity coefficients

The values of K_G, K_{KDO}, K_V and K_N for kari soils are given in Table 21. In soil 1 with high organic matter the value K_G increased from 2.18 to 40.64 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$ when the magnesium saturation of the soil was increased from 63.24 to 99.55 percentage. From Fig.16 it is clear that the increase in K_G with increase in exchangeable magnesium percentage is not linear.

The values of K_{KDO}, K_V and K_N increased to a certain extent and then decreased with increase in magnesium saturation. Their values increased upto 88.84 per cent of magnesium saturation. The value of K_{KDO} increased from 17.71 to 26.71 mol^{-1} and then decreased to a value of 4.11 mol^{-1}.

In soil 2 with relatively medium organic matter, the K_G value increased from 1.25 to 25.18 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$, when the exchangeable magnesium percentage was increased from 43.96 to 99.21. The values of all other selectivity coefficients increased upto 89.31 per cent exchangeable magnesium and then decreased. For soil 3, with low organic matter, the

Table 21 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) for Mg^{2+}- Al^{3+} system in kari soils

Exchangeable magnesium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 1		
63.24	2.18	17.71	20.19	7.87
71.26	2.60	12.99	14.37	5.78
80.89	3.73	23.81	25.42	6.82
84.84	4.55	24.19	25.48	7.70
88.84	5.89	26.71	27.74	9.36
92.66	8.14	23.85	24.45	8.61
96.37	13.49	14.01	14.24	4.37
96.87	12.38	8.59	8.68	3.82
97.87	15.57	7.08	7.13	3.14
99.55	40.64	4.11	4.12	1.83
		Soil 2		
43.96	1.25	9.81	12.06	4.36
57.08	1.74	11.22	13.09	4.98
70.10	2.42	12.89	14.12	5.12
76.83	3.17	14.49	15.71	6.44
83.12	4.24	18.59	19.70	8.26
89.31	6.16	22.63	23.45	10.05
94.16	9.01	17.13	17.47	7.03
95.10	9.22	9.26	9.42	4.11
96.48	10.74	5.89	5.96	2.62
99.21	25.18	2.31	2.32	1.03

Table 21 contd.

Exchangeable magnesium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 3		
38.18	1.14	12.81	16.14	5.69
43.64	1.98	24.31	28.72	12.45
70.65	2.91	28.60	31.71	12.71
76.75	3.59	31.00	33.60	13.77
82.99	4.70	35.48	37.61	15.77
89.09	6.73	42.04	43.63	18.69
95.19	12.96	65.97	67.04	29.33
96.04	13.99	47.02	47.66	20.90
97.34	18.28	45.59	46.00	20.28
99.42	37.99	32.65	32.71	14.51

Table 22 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient for Mg^{2+}- Al^{3+} system in laterite soils

Exchangeable magnesium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 4		
44.41	1.09	4.19	5.15	1.86
57.33	1.54	5.26	6.13	2.34
71.10	2.31	6.61	7.32	2.94
76.82	2.83	7.12	7.84	3.27
82.54	3.59	7.99	8.48	3.55
88.43	5.02	8.93	9.29	4.13
94.66	9.59	16.80	17.10	7.44
95.83	11.04	13.74	13.94	6.11
96.78	11.03	4.81	4.86	2.13
99.45	25.21	1.57	1.57	0.70
		Soil 5		
39.21	1.14	11.46	14.37	5.09
53.23	1.62	12.82	15.19	5.70
68.03	2.40	14.14	15.83	6.28
74.45	2.96	15.54	16.99	6.92
80.61	3.71	24.75	26.46	7.04
87.38	5.31	19.29	20.14	8.56
93.60	6.64	19.18	19.59	8.52
94.09	7.65	6.67	6.84	2.96
95.43	7.77	2.49	2.52	1.11
99.15	26.74	4.49	4.51	1.99

Table 22 contd.

Exchangeable magnesium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 6		
30.96	0.95	12.86	16.71	5.71
40.96	1.07	6.15	7.64	2.60
55.35	1.42	4.27	5.01	1.90
66.93	2.15	8.98	10.09	3.99
73.51	2.53	7.38	8.09	3.28
81.32	3.30	6.62	7.03	2.93
91.05	6.08	9.46	9.75	4.29
91.84	5.56	3.79	3.90	1.69
94.12	6.55	2.55	2.60	1.13
98.86	21.02	3.39	3.40	1.51

Table 23 Calculated values of Gapon selectivity coefficient (K_G), Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) for Mg^{2+}- Al^{3+} system in redloam soils

Exchangeable magnesium percentage	K_G (mol$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$)	K_{KDO} (mol^{-1} l)	K_V (mol^{-1} l)	K_N (mol^{-1} l)
		Soil 7		
35.68	0.95	6.18	7.87	2.76
44.63	1.02	2.74	3.36	1.22
61.54	1.62	3.77	4.33	1.68
69.01	2.01	4.27	4.76	1.90
77.22	2.79	6.22	6.73	2.76
84.69	3.88	6.94	7.31	3.08
91.85	5.92	5.51	5.66	2.44
93.70	6.92	4.75	4.85	2.10
95.55	8.32	2.96	3.01	1.48
99.01	20.15	1.48	1.48	0.66
		Soil 8		
33.77	0.97	9.34	11.96	4.15
49.06	1.44	11.64	14.02	5.17
62.46	1.89	8.22	9.39	3.65
70.22	2.42	10.17	11.29	4.52
77.32	3.06	10.66	11.53	4.74
84.49	4.12	8.37	11.18	4.71
90.87	5.38	5.07	5.23	2.25
92.32	5.43	2.54	2.61	1.13
94.78	7.02	2.36	2.40	1.04
98.91	19.71	1.89	1.89	0.85

Table 23 contd.

Exchangeable magnesium percentage	K_G ($mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$)	K_{KDO} ($mol^{-1}\ l$)	K_V ($mol^{-1}\ l$)	K_N ($mol^{-1}\ l$)
		Soil 9		
23.26	0.69	6.92	9.90	3.07
33.37	0.81	3.31	4.28	1.48
44.13	0.90	1.34	1.65	0.60
56.30	1.33	2.59	3.03	1.31
67.17	1.87	3.67	4.12	1.63
76.09	2.47	3.53	3.83	1.54
86.63	3.55	2.23	2.33	0.99
89.02	3.80	1.40	1.45	0.62
92.83	5.35	2.04	2.10	0.77
98.59	16.91	2.20	2.20	0.97

Gapon selectivity coefficient increased from 1.14 to 37.99 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$, when the exchangeable magnesium percentage was increased from 38.18 to 99.42. The value of other selectivity coefficients increased upto a certain extent of magnesium saturation (95.19), and further increase in exchangeable magnesium percentage decreased the values of the above selectivity coefficients.

The selectivity coefficient data for laterite soils as given in Table 22 suggests that the values obtained for these soils are comparatively less. The general shape of the magnesium selectivity curve for all the three soils are similar (Fig.17).

Soil 4 with relatively high organic matter showed an increase in K_G value from 1.09 to 25.21 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$, when its magnesium saturation was increased from 44.41 to 99.45 per cent. As in the case of other soil types the values of K_{KDO}, K_V and K_N increased upto a certain value of exchangeable magnesium percentage (94.66) and then decreased. Soil 5 with medium organic matter also showed the same trend, but the values of all the selectivity coefficients were higher for soil 5 than soil 4, suggesting a relatively higher selectivity of soil 5 for magnesium than soil 4. Here the values of K_{KDO} and K_V increased only upto 80.61 percentage

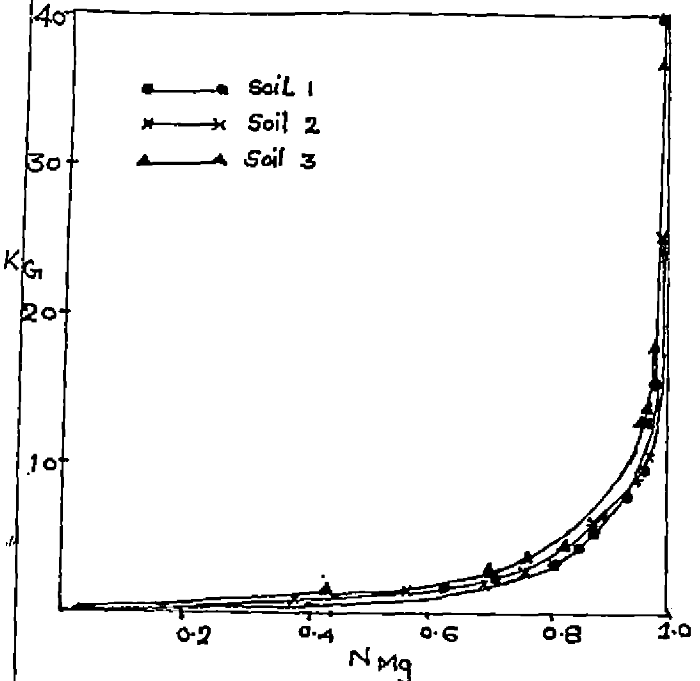

Fig. 16 Gapon Selectivity coefficient (KG) Vs. equivalent fraction of magnesium (NMg) for Mg^{2+}-Al^{3+} system in Kari soils.

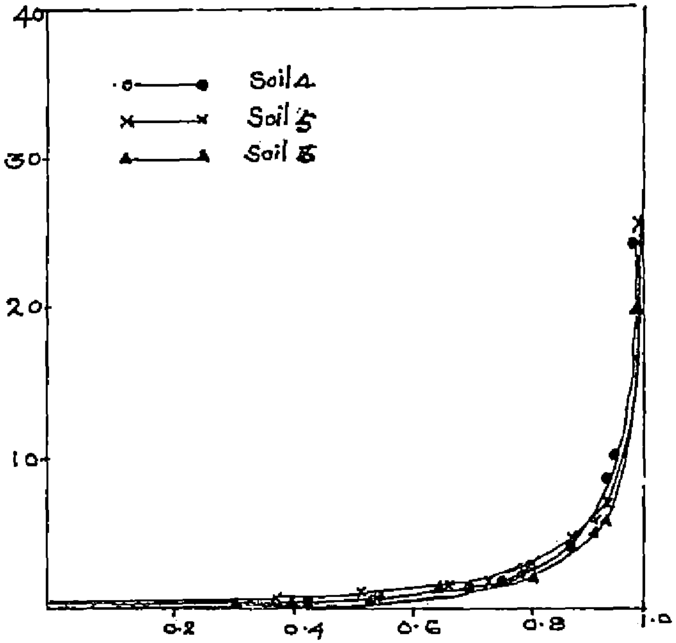

Fig. 17 Gapon selectivity coefficient (KG) Vs. equivalent fraction of Mg (NMg) for Mg^{2+}-Al^{3+} system in laterite soils

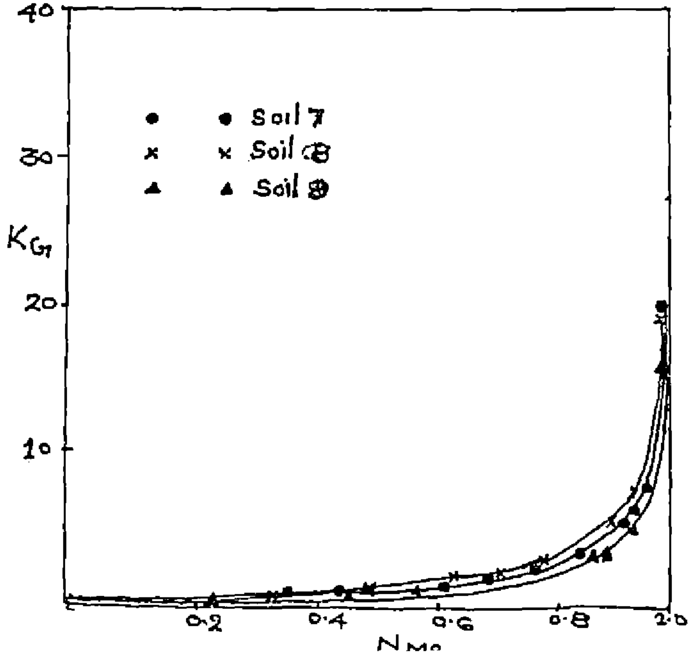

Fig. 18 Gapon selectivity coefficient (KG) Vs. equivalent fraction of Mg (NMg) for Mg^{2+}-Al^{3+} system in red loam soils

of magnesium saturation as against 94.66 per cent of soil 4.

For soil 6, the Gapon selectivity coefficient showed the same trend as observed in other soils, but the other selectivity coefficients did not show any regular relation.

The data on the calculated values of K_G, K_{KDO}, K_V and K_N for redloam soils is given in Table 23. As a result of the increase in exchangeable magnesium percentage of soil from 35.68 to 99.01, the value of K_G is found to be increased from 0.95 to 20.15 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$. The values of all other selectivity coefficients increased upto 84.69 percentage of magnesium saturation and then decreased. Compared to the kari and laterite soils, the values were lower for redloam soils, suggesting a lower selectivity of redloam soils to magnesium.

Comparing soils 7, 8 and 9, soil 8 with medium organic matter showed higher selectivity to magnesium than soils 7 and 9. For soil 8 the values of K_{KDO}, K_V and K_N increased upto 77.32 percentage of magnesium saturation and then decreased. For soil 9 the value of K_G increased from 0.69 to 16.91 $mol^{-\frac{1}{2}}\ l^{\frac{1}{2}}$, when the exchangeable magnesium percentage was increased from 23.26 to 98.59.

4.3.4. Correlation studies

Table 24 presents the data on correlation coefficients

Table 24 Values of correlation coefficient (r) for exchangeable magnesium percentage versus exchange selectivity coefficients in Mg^{2+}- Al^{3+} system

Soil	K_G	K_{KDO}	K_V	K_N
1	0.8840**	0.9182**	0.9653**	0.9744**
2	0.8676**	0.9388*	0.9791**	0.9892**
3	0.7665**	0.6560*	0.8857**	0.9168**
4	0.9398**	0.9464**	0.9748**	0.9909**
5	0.8737**	0.9182**	0.9734**	0.9853**
6	0.9135**	0.9513**	0.9856**	0.9905**
7	0.9354**	0.9610**	0.9876**	0.9937**
8	0.9191**	0.9681**	0.9896**	0.9934**
9	0.9238**	0.9605**	0.9835**	0.9935**

* Significant at 5% level

** Significant at 1% level

for the three soil types. Among the kari soils, soil 2 with medium organic matter, in general, showed the maximum correlation between exchangeable magnesium percentage and various selectivity coefficients. The dependence in general followed the order soil 2 > soil 1 > soil 3. Among the various selectivity coefficients K_N was found to be more dependent on exchangeable magnesium percentage. For soil 1 the value of r for K_N is 0.9744 as against 0.8840 for K_G.

As in the case of kari soils the exchangeable magnesium percentage dependence of selectivity coefficients is maximum for K_N and minimum for K_G in laterite soils also. For soil 4 the value of r for K_N is 0.9909 as against 0.9398 for K_G. The r value for K_G and K_N are maximum for soil 4, followed by soil 6 and soil 5. For K_{KDO} and K_V the r value is maximum for soil 6 followed by soil 4 and soil 5.

From Table 24, it is clear that the dependence of various selectivity coefficients on exchangeable magnesium percentage is maximum for redloam soils. For soil 7 with comparatively high organic matter, the value of r for K_G, K_{KDO}, K_V and K_N were 0.9354, 0.9610, 0.9876 and 0.9937, respectively.

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Table 25 Calculated values of standard free energy change (ΔG°- Cal eq^{-1}) of Mg^{2+}- Al^{3+} exchange in relation to organic matter content for Kari, laterite and redloam soils

Soil type	Organic matter content		
	High	Medium	Low
Kari	-994	-557	-1549
Laterite	-895	-980	-1001
Redloam	-831	-994	-709

4.3.5. Free energy change

The calculated values of approximate free energy change for the exchange reaction : $2\ \mathrm{Al\text{-}Soil} + 3\ \mathrm{Mg}^{2+} \rightleftharpoons 3\ \mathrm{Mg\text{-}Soil} + 2\ \mathrm{Al}^{3+}$ were negative for the three types of soils (Table 25), suggesting a strong thermodynamic preference for Mg^{2+} to Al^{3+}. The values of ΔG° for soil 1, 2 and 3 were -994, -557 and -1549 Cal eq^{-1} as against -895, -980 and -1001 Cal eq^{-1} for soil 4, 5 and 6, respectively. Among the redloam soils, the preference followed the order: Soil 8 > Soil 7 > Soil 9.

DISCUSSION

DISCUSSION

Studies were conducted to find out the effect of different electrolyte concentration on the exchange equilibrium and the influence of different cations on the free energy and various selectivity coefficients for different soils. The results obtained from the present study and some aspects on cation exchange are discussed below.

5.1. Potassium-aluminium system

5.1.1. Effect of different electrolyte concentration and organic matter levels on Al^{3+}- K^+ exchange for different soils.

From the results in Tables 2, 3 and 4 it is evident that when the soils were equilibriated with the same electrolyte concentration of aluminium, the release of potassium was maximum in Kari soils, followed by laterite soils and then by redloam soils. At an equivalent fraction of 1.00 aluminium in the equilibriating solution, soil 1 exchanged 16.41 Cmol (+) kg^{-1} of potassium as against 15.14 Cmol (+) kg^{-1} for soil 4 and 10.04 Cmol (+) kg^{-1} for soil 7. The greater adsorption of aluminium by soil 1 may be due to the high CEC of the soil 1 (38.00 Cmol (+) kg^{-1}) compared to soil 4 (23.60 Cmol (+) kg^{-1}) and soil 7 (16.20 Cmol (+) kg^{-1}).

The replacing power of Al^{3+} in relation to its concentration was found to be greater at lower concentration of the ion. For soil 1 at 0.01 equivalent fraction of Al^{3+}, it replaced 0.18 Cmol (+) kg^{-1} of K^+ as against 16.41 Cmol (+) kg^{-1} of K^+ for a 100 fold increase in solution concentration of Al^{3+}. Similar is the trend observed in other soils. This may be due to the valence effect, according to which the adsorption of higher valent ion will decrease with an increase in solution concentration.

For each soil type adsorption of aluminium and release of potassium was occurred maximum in soils, with high organic matter compared to soils with medium and low organic matter. The quantity of aluminium adsorbed by soil 1 was 16.41 Cmol (+) kg^{-1} as against 11.60 and 9.39 Cmol (+) kg^{-1} by soil 2 and 3, respectively. From this it is clear that organic matter has some influence on the availability of Al^{3+}. Using infrared techniques, Schnitzer and Skinner (1963) found that aluminium would react with organic matter upto 6:1 molar ratio, indicating six carboxyl groups per organic matter molecule. It is possible that aluminium could be electrostically bound to one or more carboxyl groups depending on the degree of polymerization and effective charge of the aluminium molecule. Clark and Nichol

(1966) also suggested the formation of insoluble aluminium organic matter complexes. It is possible that the organic matter reduces the solubility of aluminium through complex formation and results in less aluminium in the soil solution.

5.1.2. Exchange isotherms

The normalized exchange isotherms, depicting the relationship between equivalent ion fractions of Al^{3+} in the equilibrium solution and in the adsorbed phase, for all the three soil types suggested a preferential adsorption of aluminium to potassium (Fig. 1, 2 and 3). Similar results were reported for K^{+}- Al^{3+} system by Nye et al (1961) in montmorillonite and kaolinite soils, Singh and Talibudeen (1971) in nine Malaysian Ultisols and Oxisols, Pleysier et al (1979) in a Kaolinitic Ultisol and Baruah et al (1983) in some acid soils of Assam.

5.1.3. Selectivity coefficients

The Gapon selectivity coefficients data for K^{+}- Al^{3+} exchange as depicted in Fig. 4, 5 and 6 showed a higher selectivity of K^{+} than Al^{3+} for all the soils. The general shape of the K-selectivity curves was similar for all the soils. The values of the remaining selectivity coefficients

(K_{KDO}, K_V and K_N) increased upto a certain value of potassium saturation in all the soils, and then decreased (Tables 5, 6 and 7). The values of all the selectivity coefficients were in general, higher for soils with high organic matter. Among the Kari soils the K-selectivity was higher for soil 1 with high organic matter followed by soil 2 and then by soil 3, with medium and low organic matter respectively. Similar is the trend observed in laterite and redloam soils. Pleysier et al (1979) and Baruah et al (1983 a) also observed a higher selectivity for K^+ within the range of K-loading studied.

The values of the selectivity coefficients provide a good measure of the intensity factor of ion exchange reactions. A high selectivity coefficient suggests that the potassium ions are highly adsorbed in preference to the aluminium ions. It also implies that potassium can effectively replace aluminium from the soil exchanger. Nye et al (1961) also reported the effectiveness of relatively concentrated KCl solutions in displacing aluminium.

5.1.4. Correlation studies

For $K^+- Al^{3+}$ system the values of coefficients of correlation in general, were maximum for K_N and minimum for

K_G for all the soils (Table 8). The values of coefficients of correlation for K_N were significant both at 5 per cent and 1 per cent level. Except a few, there is no significant correlation between exchangeable potassium percentage and K_G, and K_{KDO}. The values of coefficients of correlation for the various selectivity coefficients in general, followed the trend $K_N > K_V > K_{KDO} > K_G$.

In general, it can be stated that the selectivity coefficients varied with exchangeable potassium percentage and organic matter content. The thermodynamic equilibrium selectivity coefficient, K_N, and Vanselow selectivity coefficient, K_V, seem to give a fair idea of the potassium-aluminium exchange. For $K^+ - Ca^{2+}$ system Mehta et al (1983) reported that K_V and K_{KDO} were dependent on potassium saturation.

5.1.5. Free energy change

The negative values of the approximate free energy change (ΔG°) for the exchange reaction: Al-soil + $3K^+$ 3K-soil + Al^{3+}, for the whole exchange isotherm (Table 9) suggested that the reaction was spontaneous, showing higher preference of K^+ to Al^{3+}. Among the three soil types red-loam soils showed the maximum thermodynamic preference for potassium, followed by laterite soils and then by kari soils. Comparing soils 1, 2 and 3 on the basis of organic matter it can be seen that soil 3 with low organic matter showed the maximum preference for potassium, followed by soil 2 and then by soil 1. Similar is the trend observed in other soil types.

Singh and Talibudeen (1971) also reported negative values of $\triangle G^\circ$ for seven of the nine soils they studied at a total electrolyte concentration of 0.1 N. They explained that the small K^+-ion (4 A°) is bound more strongly than $Al\ (H_2O)_6^{3+}$ (8 A°) in these soils since it presumably can approach the surface more closely resulting in a stronger electrostatic force of attraction. Similar results were also reported by Pleysier et al (1979) and Baruah et al (1983 a). In the latter, it has been described that the higher preference of potassium to aluminium was presumably due to the presence of dioctahedral mica together with vermiculite and smectite in the soils. These minerals are known to be more selective for potassium than aluminium.

The results of this investigation lead to the conclusion that potassic fertilizers can be used effectively in these soils because of their high retention and minimum leaching losses. However, it is not advisable to apply the entire dose of potassic fertilizers in a single dose to extremely acidic organic soils with high aluminium content.

5.2. Calcium-aluminium system

5.2.1. Effect of different electrolyte concentration and organic matter levels on Al^{3+}- Ca^{2+} exchange for different soils

As in the case of K^{+}- Al^{3+} exchange, here also the adsorption of aluminium (and desorption of calcium) increases with increase in electrolyte concentration of aluminium. But compared to the K^{+}- Al^{3+} exchange the release of calcium was less for all the soils (Tables 10, 11 and 12). The trivalent aluminium with high bonding energy replaces the monovalent potassium more strongly in K^{+}- Al^{3+} exchange than the divalent calcium in Ca^{2+}- Al^{3+} exchange. At an equivalent fraction of 1.00 aluminium in the equilibriating solution soil 1 replaced 16.41 Cmol (+) kg^{-1} of K^{+}- Al^{3+} exchange as against 14.30 Cmol (+) kg^{-1} of Ca^{2+} in Ca^{2+}- Al^{3+} exchange.

Compared to the kari soils the release of adsorbed ion was less in laterite and redloam soils. At the same equivalent fraction of aluminium (1.00) in the equilibriating solution the quantity of calcium desorbed by kari soil was 14.30 me/100 g as against 13.58 and 11.02 me/100 g by laterite and redloam soils, respectively. This may be due to the difference in organic matter content and cation exchange capacity. Within each soil type maximum desorption of calcium occurred in soils with high organic matter, suggesting a greater tendency of these soils to adsorb more aluminium. This observation was in confirmity with the findings of Evans and Kamprath (1971) and Carbrera and Talibudeen (1977). They reported a low aluminium concentration in the soil solution of organic rich acid soils. Hoyt and Turner (1975) reported that adding alfalfa meal, sucrose and peat moss to very acid soils decreased toxic quantities of exchangeable aluminium. This was attributed to complexing of exchangeable aluminium by organic matter.

5.2.2. Exchange isotherms

The normalized exchange isotherms of aluminium for all the three soil types lay above the diagonal (Fig. 7, 8 and 9), showing the preferential adsorption of aluminium to calcium. It is clear from the Figures that the redloam soils showed the maximum preference for aluminium followed by laterite soils and then by kari soils. Baruah et al (1983 a) also reported similar results from their studies on Al-Ca exchange in some acid soils of Assam.

5.2.3. Selectivity coefficients

The values of all the selectivity coefficients for Ca^{2+}- Al^{3+} system (Tables 13, 14 and 15) followed the same trend as obtained in K^{+}- Al^{3+} system but the values were much lower. This suggested that the soils showed a decreasing selectivity for calcium compared to potassium in the presence of aluminium. Among the three soil types, kari soils showed the maximum selectivity for calcium, followed by laterite and then redloam soils. The present data differ considerably from those published by Pleysier et al (1979) who found a strong selectivity of aluminium over calcium. They explained that the higher selectivity for aluminium at low aluminium loading could be due to the presence of high energetic sites. Baruah et al (1983 a), however, observed a decreasing aluminium selectivity with increasing calcium saturation in some acid soils of Assam.

5.2.4. Correlation studies

Compared to the K^{+}- Al^{3+} system the values of coefficients of correlations for all the selectivity coefficients for Ca^{2+}- Al^{3+} system were higher (Table 16). The dependence of various selectivity coefficients on exchangeable calcium percentage followed the same trend as observed in K^+- Al^{3+} system ($K_N > K_V > K_{KDO} > K_G$). The values of r for various selectivity coefficients, in general, were higher for soils with high organic matter compared to soils with medium and low organic matter. As in the case of K^+- Al^{3+} system, here also K_G was found least dependent on exchangeable calcium percentage. So the highly correlated coefficients viz. K_N and K_V may be preferable in studying the exchange phenomena in these soils.

5.2.5. Free energy change

The weighted mean value of the approximate free energy change for the exchange reaction: 2Al-soil + 3 $Ca^{2+} \rightleftharpoons$ 3 Ca-soil + 2 Al^{3+}, for the whole exchange isotherms (Table 17) suggested that the reaction was spontaneous, showing higher preferences of calcium to aluminium for all the soils. But compared to the K^+- Al^{3+} system the values were much lower for all the soils. For soil 1 with high organic matter the free energy change (ΔG°) amounts $^{-}905$ Cal eq^{-1} for Ca^{2+}- Al^{3+} system as against $^{-}2303$ Cal eq^{-1} for K^+- Al^{3+} system. Similarly, for laterite soil (soil 4) the corresponding values were $^{-}936$ and $^{-}2636$ Cal eq^{-1}, respectively, for Ca^{2+}- Al^{3+} and K^+- Al^{3+} system.

Talibudeen (1981) and Baruah et al (1983 a) observed positive values of free energy change for Ca-Al exchange as against the negative values observed in the present study. They explained that trivalent aluminium has an octahedrally co-ordinated water sheath, so tightly held to the central ion that the structural entity binds adjacent oxygen layers more strongly than the divalent calcium ion. The lower selectivity of aluminium compared to calcium in the present study may be due to the hydrolysis of aluminium. As a result of hydrolysis the total valency of aluminium in the solution will decrease. This will inturn help in the greater adsorption of calcium compared to aluminium.

From this study it is clear that compared to potassium calcium is held by the soil with less energy. Though calcium is preferentially adsorbed over aluminium, the energy with which it is adsorbed is much less compared to potassium. So to maintain a high concentration of calcium in these soils, frequent application of lime becomes necessary.

5.3. Magnesium-aluminium system

5.3.1. Effect of different electrolyte concentrations and organic matter levels on Mg^{2+}- Al^{3+} exchange for different soils

Tables 18, 19 and 20 present the data on the equilibrium concentration of aluminium and magnesium for Mg^{2+}- Al^{3+}

exchange in kari, laterite and redloam soils, respectively. The data did not differ much from that of Ca^{2+}- Al^{3+} system, but it differs considerably from that of K^{+}- Al^{3+} system. At the maximum equivalent fraction of Al (1.00) in the equilibriating solution soil 1 adsorbed 13.97 Cmol (+) kg^{-1} of aluminium for Mg^{2+}- Al^{3+} exchange as against 14.30 and 16.41 Cmol (+) kg^{-1} for Ca^{2+}- Al^{3+} and K^{+}- Al^{3+} exchange, respectively. Similar is the trend observed in other soils.

Comparing the soils on the basis of organic matter content, it can be seen that soils with high organic matter adsorbed more of aluminium than the one with medium and low organic matter. Soil 4 with 23.60 Cmol (+) kg^{-1} CEC and 6.12 per cent organic matter adsorbed 13.12 Cmol (+) kg^{-1} of aluminium as against 10.42 Cmol (+) kg^{-1} by soil 7, with 16.20 Cmol (+) kg^{-1} CEC and 5.45 per cent organic matter.

5.3.2. Exchange isotherms

From Fig. 13, 14 and 15 it is clear that all the nine soils showed higher preference for aluminium compared to magnesium. But, compared to the K^{+}- Al^{3+} system the preference for aluminium is less in Mg^{2+}- Al^{3+} system. Exchange isotherms of aluminium for Ca^{2+}- Al^{3+} and Mg^{2+}- Al^{3+} followed the same pattern and did not differ much. Comparing the three systems the exchange isotherms show a sequence of preferential adsorption which follows the order: Al > Ca > Mg > K. Pleysier et al (1979) reported the following order of preference: Al > Ca > K > Na for exchange equilibria involving aluminium, calcium, potassium and sodium. Baruah et al (1983 a) observed the sequence of preferential adsorption which follows the order: Al > Ca > NH_4 > K.

5.3.3. Selectivity coefficients

The values of all the selectivity coefficients were more or less same as that obtained for $Ca^{2+}- Al^{3+}$ system for all the soils. In general, the magnesium selectivity was higher for kari soils, followed by the laterite soils and then by the redloam soils. Comparing the three systems ($K^{+}- Al^{3+}$, $Ca^{2+}- Al^{3+}$ and $Mg^{2+}- Al^{3+}$) it can be seen that the selectivity for all the nine soils is maximum for potassium. The selectivity for calcium and magnesium is more or less same. The selectivity sequence as indicated by selectivity coefficients for all the soils follows the order: K > Ca $\gg$ Mg > Al. For ion exchange equilibria involving aluminium, potassium, calcium and sodium, Pleysier et al (1979) observed the following selectivity sequence: K > Al > Ca > Na.

The preference sequence observed earlier differed considerably from the selectivity sequence. The preference of an ion exchanger for one of the two counter ions is determined by the ratio of the equivalent fraction of the two counter ions in the exchanger and the equilibrium solution. For the heterovalent exchange, it is strongly dependent on the solution concentration (Helfferich, 1962). The apparent contradiction between the preference sequence and the selectivity sequence is therefore due to the concentration-valency effect.

5.3.4. Correlation studies

As in the case of Ca^{2+}- Al^{3+} system, it is clear from Table 24 that the coefficients of correlation (r) for K_G, K_{KDO}, K_V and K_N were significant at both levels. The values in general, were more or less similar to that obtained for Ca^{2+}- Al^{3+} system. For all the soils the value of r for K_N was found to be maximum. The dependence of various selectivity coefficients on exchangeable magnesium percentage followed the order: $K_N > K_{KV} > K_{KDO} > K_G$. In general, the values of r for various selectivity coefficients were greater for soils with higher organic matter.

5.3.5. Free energy change

The negative values of free energy change for the exchange reaction: $2\ \mathrm{Al\text{-}soil} + 3\ \mathrm{Mg}^{2+} \rightleftharpoons 3\ \mathrm{Mg\text{-}soil} + 2\ \mathrm{Al}^{3+}$ suggested a strong thermodynamic preference for magnesium to aluminium (Table 25). The values for all the nine soils were lower than that obtained for K^{+}- Al^{3+} system. Comparing the values of free energy change for Mg^{2+}- Al^{3+} system and Ca^{2+}- Al^{3+} system, it can be seen that, they were more or less same. In general, soils low in organic matter showed the maximum thermodynamic preference for magnesium. This indicated that soils with high organic matter showed a greater preference for aluminium compared to magnesium.

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSIONS

The ratios of cations in the adsorbed phase and in the soil solution are of utmost importance in determining their behaviour in different soils. Acid soils in high rainfall areas suffer from deficiency of nutrients, especially calcium and magnesium, and accumulation of aluminium ions in the adsorbed phase. The present investigation was conducted to study the exchange equilibria involving aluminium, potassium, calcium and magnesium in some acid soils of Kerala. For this purpose soil samples differing in their organic matter content and texture were collected from several locations. This included kari, laterite and redloam soils. The soil samples were made homoionic with potassium, calcium and magnesium by repeated washing with their chloride solutions. The homoionic samples were then equilibriated with chloride solutions of K + Al, Ca + Al and Mg + Al, respectively, at 10 different equivalent ion fractions of aluminium at a total electrolyte concentration of 20 me l^{-1} for each ion pair. The equilibrium concentration of cations in the solution and adsorbed phases were determined. The data were interpreted in terms of normalized exchange isotherms, various selectivity coefficients, free energy changes of the exchange reactions etc.

The significant results obtained and the important conclusions drawn are listed below:

1. From the study on the effect of different electrolyte concentrations on aluminium-potassium exchange, it was observed that with increase in the electrolyte concentration of aluminium more of aluminium was adsorbed by the soil and an equivalent amount of potassium was displaced into the soil solution.

2. The adsorption of aluminium was maximum in soils with high organic matter content. Thus kari soil with high organic matter content adsorbed the maximum quantity of aluminium and the redloam soil, with low organic matter adsorbed the lowest quantity of aluminium.

3. The normalized exchange isotherms of aluminium for K^+-Al^{3+} system in kari, laterite and redloam soils suggested the preferential adsorption of aluminium to potassium in all the three soil types.

4. For all the three soil types the values of Gapon selectivity coefficient (K_G) increased with increase in exchangeable potassium percentage, suggesting an increased selectivity for potassium with increase in exchangeable potassium percentage.

5. The values of the remaining selectivity coefficients, namely Krishnamoorthy-Davis-Overstreet selectivity coefficient (K_{KDO}), Vanselow selectivity coefficient (K_V) and equilibrium selectivity coefficient (K_N) increased upto a certain value of exchangeable potassium percentage and then decreased.

6. The values of all the selectivity coefficients were, in general, higher for kari soil followed by laterite and red-loam soils. This suggested an increased selectivity of soils for potassium with increase in organic matter.

7. In all the soils, the equilibrium selectivity coefficient (K_N) in general, showed the maximum dependency to potassium saturation. The dependency, in general, followed the order: $K_N > K_V > K_{KDO} > K_G$.

8. The negative values of free energy change for the exchange reaction: $Al\text{-}soil^{+} 3K^{+} \rightleftharpoons 3K\text{-}soil + Al^{3+}$ suggested the preferential adsorption of potassium to aluminium in all the soils. Comparing soils on the basis of free energy, redloam soils with low organic matter showed the maximum thermodynamic preference for potassium, followed by laterite and kari soils.

9. As in the case of $K^{+}\text{-}Al^{3+}$ system, the adsorption of aluminium by soil solid increased with increase in the solution concentration of aluminium in $Ca^{2+}\text{-}Al^{3+}$ system also.

10. Compared to the K^+-Al^{3+} system the amount of aluminium adsorption was less in calcium-aluminium system.

11. The effect of organic matter on Ca^{2+}-Al^{3+} exchange was similar to that observed in K^+-Al^{3+} system.

12. For all the soils, the normalized exchange isotherms of aluminium lay above the diagonal, suggesting a higher preference for aluminium to calcium.

13. Similar to the K^+-Al^{3+} system the values of K_G increased with increase in calcium saturation. The remaining selectivity coefficients increased upto a certain value of calcium saturation and then decreased with further increase in calcium saturation.

14. Compared to the K^+-Al^{3+} system, the values of all the selectivity coefficients were lower, thereby showing a lower selectivity for calcium compared to potassium in the presence of aluminium.

15. The various selectivity coefficient showed higher correlation with exchangeable calcium percentage than with exchangeable potassium percentage.

16. The weighted mean values of the free energy change for the exchange reaction $2Al\text{-}Soil + 3Ca^{2+} \rightleftharpoons 3Ca\text{-}Soil + 2Al^{3+}$ were

negative. However, the values were smaller than that obtained for K^+-Al^{3+} exchange. This indicates a lower thermodynamic preference for calcium compared to potassium in the presence of aluminium.

17. For Mg^{2+}-Al^{3+} system the results obtained were more or less similar to that obtained for Ca^{2+}-Al^{2+} system.

18. Correlation studies have shown that the thermodynamic equilibrium coefficient, K_N, and the Vanselow selectivity coefficient, K_V, can be effectively used in describing the ion exchange phenomena in the acid soils of Kerala, as these two coefficients showed the maximum correlation with the exchangeable cations.

19. Among the three cations, potassium, calcium and magnesium, magnesium was less preferentially adsorbed compared to potassium and calcium in the presence of aluminium.

20. The values of free energy change showed the following order of preference for the competing cations: K > Ca > Mg > Al.

On the basis of the present study, it can be concluded that potassic fertilizers can be effectively used in acid soils of Kerala, because of its high retention and minimum leaching loss. Though calcium and magnesium were preferentially adsorbed over aluminium by the soils, to maintain a higher concentration of these cations in the exchange phase, a considerable amount of calcium and magnesium should be supplied by frequent application of lime; as these two cations are held with much less bond energy compared to potassium. To evaluate correctly the response of applied potassic fertilizers and liming material in different soils, efforts should be made to relate exchange behaviour of potassium, calcium and magnesium to the nature and relative proportion of different soil clay minerals. Similarly, the extension of the predictive approach essentially meant for binary systems need special attention in order to make the studies on cation exchange equilibria more realistic and field oriented.

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ABSTRACT

More than 70 per cent of the upland soils of Kerala are acidic. The acidity of the soil is primarily associated with the presence of hydrogen and aluminium in exchangeable form. The soil solution aluminium in acid soil infertility clearly establishes the agronomic significance of aluminium ion equilibria in soils. The present study, entitled "Studies on exchange equilibria and its prediction on some acid soils of Kerala" was conducted to find out (1) the effect of different concentrations of aluminium in the electrolyte solution on exchange equilibria in soils (2) the influence of different cations on the free energy and various selectivity coefficients (3) the dependence of different selectivity coefficients on potassium, calcium and magnesium saturation of soils (4) the role of organic matter on cation exchange equilibria with special reference to potassium, calcium, magnesium and aluminium.

Cation exchange equilibria involving aluminium-potassium, aluminium-calcium and aluminium-magnesium were studied in three soil types, viz., Kari, laterite and redloam soils, differencing in their texture and organic matter content. The normalized exchange isotherms for different soils and

cationic systems were drawn and the results were interpreted in terms of different selectivity coefficients and approximate free energy change of the exchange reactions.

From the study on the effect of different electrolyte concentration of aluminium on aluminium-potassium, aluminium-calcium and aluminium-magnesium exchange, an increasing aluminium adsorption was observed with an increase in electrolyte concentration of aluminium. The adsorption of aluminium was maximum in soils with high organic matter content.

The normalized exchange isotherms of aluminium for different cationic systems and soils lay above the diagonal, suggested the preferential adsorption of aluminium over other cations.

Except the Gapon selectivity coefficient, all the other coefficients (K_{KDO}, K_V and K_N) increased upto a certain value of base saturation and then decreased. The value of K_G increased with increase in base saturation. Among the various selectivity coefficients, K_N was found to be the most dependent one and K_G the least dependent. The dependence followed the order $K_N > K_V > K_{KDO} > K_G$.

The negative values of free energy change for different cationic systems suggested the preferential adsorption of potassium, calcium and magnesium over aluminium. Among these cations potassium was found to be adsorbed with more energy, followed by calcium, magnesium, and then by aluminium. The values of free energy change showed the following order of preference for the competing cations: K > Ca > Mg > Al.

From the study it can be concluded that potassic fertilizers can be effectively used in acid soils of Kerala, because of its high retention and minimum leaching loss. Compared to potassium, calcium and magnesium were adsorbed with less bond energy and hence to maintain a higher concentration of these cations in the soil exchanger, a considerable amount of calcium and magnesium should be supplied by frequent application of lime. To evaluate correctly the response of applied potassic fertilizers and liming material in different soils, efforts should be made to relate exchange behaviour of potassium, calcium and magnesium to the nature and relative proportion of different soil clay minerals. Similarly, the extension of the predictive approach essentially meant for binary system need special attention in order to make the studies on cation exchange equilibria more realistic and field oriented.