CHAPTER I

SECTION A

Introduction and Review of Previous Work

Plant roots take up ions as nutrients from the soil by a process of ion exchange. In this process, the clay fraction of the soil plays a significant and vital role. Hence, a study of the exchange characteristics of clay fraction reveals, generally, the exchange behaviour of the soil as a whole. The colloidal properties of clay minerals have been used for hundreds of years, especially in the manufacture of pottery and in foundry. A systematic attempt has, however, been made only in this century to understand the origin of their behaviour. But even then the surface and colloid chemistry of clays have not been adequately investigated. Considerable success has been achieved in the past fifty years in regard to the search for high purity clays and for evidences of their crystallinity. The atomic structures of the common clay minerals have been to a great extent determined, and applied to explain the properties of the individual members by numerous investigators.

The structures of some of the clay minerals used in the present investigation are briefly discussed, indicating their differences from each other and their peculiarities, which are responsible for the special colloidal behaviour of

the minerals. Clay minerals viz. kaolinite, montmorillonite, illite, chlorite and vermiculite and mixed layer-lattice type minerals have been identified in the vast majority of natural soils.

The correlation between the structure and exchange properties of these minerals has been established from a crystallo-chemical point of view on the basis of the important contributions of Pauling (1), Bragg (2), Gruner (3), Brindley (4), Hofmann (5), Marshall (6), Hendricks (7) and others (8), (9), (10), (11), (12), (13), (14). From these studies clay minerals are recognised to consist essentially of two structural units. One is composed of two sheets of closely packed oxygens or hydroxyls in which aluminium or magnesium atoms are arranged in octahedral coordination, so that they are equidistant from six oxygens or hydroxyls. With aluminium in the octahedral position, only two-thirds of the possible positions are filled to balance the structure. It is the gibbsite structure having the formula $Al_2(OH)_6$. When magnesium is present, all the possible positions are filled to balance the structure giving the brucite structure which has the formula $Mg_3(OH)_6$.

The second unit is the tetrahedrally co-ordinated silica. A silicon atom being placed at the centre of a tetrahedron is equidistant from four oxygens or hydroxyls. The silica

tetrahedra are joined together in the a,b-directions, through oxygen, to form a hexagonal network which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$. The tips of all the tetrahedra are in the same direction.

Kaolinite: The kaolinite is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedra and one of the layers of the octahedral sheet form a common layer. All the tips of the silica tetrahedra point in the same direction and toward the centre of the unit made of the silica and octahedral sheets. These sheets which are continuous in the a,b-directions are stacked one above the other in the c-direction. During stacking the oxygens of the tetrahedral layer are placed very close to the hydroxyls of the octahedral layer, so that the sheets are held tightly by hydrogen bonding as a result of which very little expansion in the c-direction is possible.

Montmorillonite: According to the currently accepted concept, montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedrons point in the same direction and toward the centre of the unit. The tetrahedral and octahedral

sheets are combined so that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to the tetrahedral and octahedral layers become O instead of OH.

The minerals of this group are also developed by stacking of these unit sheets one above the other in the c-direction. During stacking the O layers of one unit are close to the O layers of the other unit, so that there is an excellent cleavage between the sheets. Polar molecules can enter the space between the sheets causing expansion of the axis in the c-direction. Isomorphous substitution of other metal ions for silicon and aluminium in both the tetrahedral and octahedral layers is known to occur. Complete replacement of aluminium by iron and magnesium is found in the minerals nontronite and saponite respectively. Substitution in the tetrahedral layer in montmorillonite does take place but to a limited extent.

Vermiculite: It consists of alternate stacking of mica and water layers. Isomorphous replacement of Al for Si always takes place in the tetrahedral layer and replacement of Fe or Mg for Al in the octahedral layer is limited. In natural vermiculites the net resulting charge deficiency is balanced primarily by Mg^{2+} and to some extent by Ca^{2+}. These ions are held as exchangeable ions in between the mica layers. It has also been

suggested that these exchangeable ions are responsible for the orientation of water molecules. The Mg^{2+} are present in octahedral grouping with six water molecules causing the existence of two layers of water molecules, but with K^{+} in place of Mg^{2+} the thickness of water layer is monomolecular. The c-axis expansion is limited to the thickness of two water molecules.

Laponite: One of the better known natural swelling clays is the mineral hectorite. This substance occurs heavily contaminated with other minerals such as dolomite and quartz which are not easily removed. In addition, the deposits of hectorite are limited.

Laponite, being a manufactured product, provides, for the first time, a reliable consistent supply of high purity swelling clay. In addition, the material has a number of other important properties not found in its natural equivalent.

Laponites are magnesium silicates with a layered structure, and are obtained as granular, free-flowing white powders. When the powders are dispersed in water they form thixotropic gels. The layered structure of these products is identical to that of natural hectorite. Hectorite is the trioctahedral equivalent of montmorillonite and owes its charge to octahedral replacements of Mg by Li. Its structural formula is

$$\overline{\langle Si_8 \rangle}^{IV} \; \overline{\langle Mg_{6-x} \underset{\downarrow}{Li_x} \rangle}^{VI} \; O_{20}(OH)_4$$

$$Mx$$

The charge x is of the order of 0.6 to 0.7 valences per unit cell. The structural formula of Na-Laponite CP is :

$$Na_{0.70} \; (Mg_{5.26}, \; Li_{0.59}) \; Si_{8.01} \; O_{24}H_{3.97}$$

In certain of the Laponite products, there are no fluorine atoms in the structure, these being replaced by hydroxyl ions. The layers (platelets) are about a Nanometer (10Å) thick and extend in two dimensions. If the only cations present were silicon and magnesium, a single layer would be electrically neutral. However, since some magnesium is substituted by lithium and some structural positions normally occupied by these cations may be unoccupied, these layers have a negative charge which is balanced by exchangeable cations — normally sodium ions — situated outside the structure, between the multiple layers.

An important phenomenon exhibited by clay minerals is their property of sorbing cations and retaining these in an exchangeable state. This can be explained by considering the existence of a net negative charge of clay particles at all pH

values above two or three which is compensated by the presence of positive counterions. They form negatively charged micelles in contact with water and either adsorb cations from the dispersion medium or dissociate ions which are adsorbed in its structure, thus exhibiting ion exchange reactions (15,16). Ion exchange sorption of inorganic as well as organic ions is known to occur on clay minerals. Hence the origins of this charge on the clay lattice are believed to be due to isomorphic substitution, lattice imperfections, broken bonds at the edges of the particles and exposed structural hydroxyls.

The negative charge on the clay minerals is compensated by adsorption of cations. The counterions are held on the external surfaces of the aggregates and between the unit layers in clays which swell in aquous suspension, whereas the sorption of counterions takes place onto the external surfaces only in non swelling clays. In aquous suspension, some of these cations remain in a closely held stern layer; others diffuse away from the surface and form a diffuse double layer. Provided that they are not fixed by engaging in strong, specific bonding with the clay or by being trapped between unit layers that have collapsed together irreversibly (lattice collapse), the counterions can undergo ion exchange with other cations present in the system. The magnitude of the cation exchange capacity of a clay depends largely on the type of clay and to a lesser extent on the source of a particular sample.

The experimentally measured specific surface area of a clay mineral depends on the type of clay and the method of measurement employed; among clays of the same type the values vary from sample to sample, and in any one mineral sample the nature of the counterions present may influence the measured surface area. The theoretical surface areas were calculated from the weights of the unit cells, and their dimensions as indicated by x-ray diffraction.

Systematic studies of cation exchange in pure clay minerals were carried out by Page and Baver (17), Bar and Denderloo (18), Hendricks and Alexander (19), Schachtschabel (20), Mukherjee (21) and others. Most of these investigations were based upon exchange equilibria, selectivity etc. with simple inorganic ions (22,23). Exchange reactions involving clay minerals with organic compounds have also been established by different scientists (24,25,26,27), but study on the adsorption and desorption of inorganic trivalent complex cations (28, 29) is rather meagre. The physico chemical aspects of many of these reactions, being still unknown in their fundamental details, constitute one of the objectives of the present investigation. The relevant literature has been reviewed below.

Amongst earlier workers, Renold (30) (1936) was perhaps the first to study systematically the exchange behaviour of Cu, Pb, Ni, Ag, Zn, Hg and Cd- permutites and observed an increase

in the exchangeability of these cations in the order shown. Zn was found by him to be as effective as Ba in its exchanging power. Jeny and Engabaly (31) (1943) showed, on the basis of the exchange characteristics of zinc-montmorillonite that Zn ion is partially rendered non-exchangeable by being co-ordinated to the clay mineral. Basu and Mukherjee (32,33) have studied in detail the interaction of montmorillonite clay and trace element cations. They observed the release of the metal ions in the order : $Zn^{2+} > Mn^{2+} > Ni^{2+} = Co^{2+} > Cu^{2+}$ from the clay surface by H^{+}. Moreover, quantitative measurements revealed that the amount released was much less than that adsorbed, so that a part of the adsorbed cations was considered to be 'fixed'. Martin and Claesar (34) studied the adsorption of $Co(NH_3)_6Cl_3$ on montmorillonite under various pH conditions. They found that it also permits the estimation of the internal and external exchange capacities. Connel and Maatman (35) from a study of the interactions of the complexes of Co(III) in the pores of silica gel could measure the pore volume of a high surface area silica gel. A continuous extraction of recoil products from the Szilard-Chalmers reaction on hexammine cobaltic ion and tris ethylene diamine cobaltic ion adsorbed on an ion exchange resin has been proposed for obtaining a high yield and specific activity (36). The Szilard-Chalmers reaction is usually studied

batchwise, i.e., some suitable compounds are irradiated with neutrons and then the new species produced by recoil are separated from the parent by some chemical procedure. For the best results in this process the stability of the complex ion towards the eluant should be high and both the resin and the complex ion should be resistant to radiolysis and the radiolytic products from the eluant. A cation exchange resin loaded with hexammine cobalt (III) ion or tris ethylene diamine cobalt (III) ion is suitable for this method, because these complex ions give rise to the bivalent cobaltous ion upon neutron irradiation (37-40). The retention of hexammine cobalt ion is, however, found to be lower than the corresponding value for the tris ethylene diamine cobalt ion using the dynamic method (36). Chakravarti and Laitinen (41) studied sorption and desorption of $Coen_3Cl_3$ on Pyrex glass. The exchange capacity determined from the exchange of $[Co^{*}en_3]^{3+}$ agreed well with those obtained from the sorption and desorption studies of $Cr^{*}_{51}{}^{3+}$ and $Cs^{*}_{137}{}^{+}$. Das Kanungo, Chakravarti and Mukherjee (42,43,44) studied adsorption and desorption of hexammine cobalt (III) chloride and tris ethylene diamine cobalt (III) chloride on bentonite and vermiculite and observed that adsorption is according to Langmuir's equation and the desorbing cations arrange themselves according to the lyotrope series. Recently V.J.Thielmann and J.L. McAtee, Jr. (45) investigated the gas chromatographic behaviour of metal-tris (ethylene diamine) complex cation-

exchanged montmorillonites for the separation of oxides of nitrogen and light hydrocarbons and showed that N_2O is involved in an adsorption process on the oxygens of the basal surface of the clay, whereas the light hydrocarbons were most probably involved in a sieving separation. The cation exchange process between tris (ethylene diamine) cobalt (III) and Na^+ on montmorillonite has been studied by M.I. Knudson, Jr. and J.L. McAtee, Jr. (46) and concluded that the exchange of $Co(en)_3^{3+}$ for Na^+ was found to be extremely favourable, with a tendency toward segregation of the two kinds of cations in the mixed clays studied. The studies on exchange characteristics of Zeolites, either synthetic or natural by Barrer (47) and others have received a great deal of attention in recent years. R.M.Barrer and R.P.Townsend (48) studied the exchange of cuprammine and zincammine ions in ammonium forms of clinoptilolite, mordenite and phillipsite in ammoniacal solution, pH > 10, and similar investigations are reported on the $\left[Co(NH_3)_6\right]^{3+}$ ion at pH values of ~ 5 and ~ 10 in mordenite. Isotherms were too rectangular to calculate values of the standard free energy of exchange, and selectivities were very much higher than for the corresponding aquo ions in mordenite at low pH. Barrer et al concluded that the increase in selectivities observed with mordenite when the cobalt, copper and zinc ions were complexed with ammonia might be rationalised in terms of dielectric theory.

From the study of the reactions between organic compounds and different types of clays made by a large number of workers, the specific nature of clay mineral-organic ion reactions has now been fairly well established. Thus, Smith (49), Gieseking (50) and his Colleagues (51,52) definitely showed from their work with different organic bases and their salts, and with gelatin and albumin solutions, that organic ions enter into cation exchange reactions with clay minerals, particularly montmorillonite. The adsorption of primary n-alcohols (C_2-C_9) from dilute aquous solutions by calcium and sodium montmorillonite has been studied by German and Harding (53) and they reported that the lower members of the series were adsorbed to an appreciable extent. This behaviour seems to be at variance with the earlier observations of Hoffmann and Brindley (54) who reported that polar compounds with chain lengths less than six units were not measurably adsorbed by calcium montmorillonite. Mac Ewan (55) was the first to study the formation and properties of complexes between ammonium montmorillonite and an homologous series of primary n-alcohols. He observed that except for methanol and ethanol, both of which gave a double layer complex, primary aliphatic alcohols formed single-layer complexes with the alkyl chain lying parallel to the silicate layer. Subsequently, Barshad (56) also reported similar observation for calcium montmorillonite. Brindley and Ray (57) studied

complexes of calcium-montmorillonite with even numbered straight chain alcohols with 2 to 18 carbon atoms and observed four series of basal spacing. They conclude that mono - and bilayers are formed between the unit layers of the clay with the chain of the alcohol parallel to the surface of the clay and suggest that hydrogen bonds are formed between alcoholic hydroxyls and siloxance oxygene. Glaesar (58) and Mac Ewan (55) were among the first to prepare complexes of montmorillonite with ketones. By treating the clay with a large excess of acetone and nitrobenzene, with or without boiling, Mac Ewan was able to form two layer complexes with calcium and ammonium motmorillonite, respectively. Motmorillonite with alkyl ammonium or pyridine-type counterions has only one or two layers of water between the unit layers in aquous suspension, compared to four and greater than 30, for the analogous calcium and sodium substituted clays, respectively (59-61). It was also observed by Slabaugh and Carter that the hydrophobicity of an organoclay increases with increasing size of the organic counterion (62). A pyridinium montmorillonite was found to adsorb five times as much benzene vapour as the sodium clay from which it was made (63). Alkyl ammonium montmorillonites swell in most organic solvents (64). The adsorption of amino acids and peptides on H-montmorillonite shows a Langmuir type isotherm; such adsorption occurs primarily through ion exchange of the protonated molecules, although a small amount of the organic molecule

is adsorbed beyond the cation exchange capacity (65). Thermodynamic data show that the negative free energy of exchange of n-alkyl ammonium ions on sodium montmorillonite increases with increasing chain length (66). This indicates not only the clay-cation interaction, but also interactions between the alkyl chains of these cations.

R.K.Schofield (67) observed that the adsorption of quaternary ammonium cations on kaolinite is sufficiently strong to reverse the charge on the particles from negative to positive.

Thorough investigations by other workers (68-70) have also been made specially on the interaction between organic molecules and clays. Our knowledge of the desorption of inorganic cations from the clay surface by organic ions is still meagre. It is in this context that an attempt has been made in the present investigation to study the sorption and desorption characteristics of some trivalent inorganic complex ions by a number of inorganic and organic cations of varying sizes and shapes.

SECTION B

Ion-Exchange Formulations.

A number of approaches (71), both qualitative and quantitative, have been made to understand the equilibria between an ion-exchanger and ions in solution. Experiments were performed in which concentrations of ions were varied, the result suggested an exponential relationship between the ions adsorbed (or desorbed) and concentration of the exchanging ions. Limitations have been tacitly accepted in most mathematical treatments of exchange reactions. Thus (i) the simultaneous presence of both cation and anion exchange reactions in a given system has been considered rarely, (ii) the exchange capacity of the cation or anion exchanger has been assumed to be constant, though cases are known where the exchange capacity varies markedly with the pH and the nature of the exchanging ion, (iii) simple stoichiometric equivalence between ions taken up and released is generally assumed to be present; deviations are usually explained in terms of simultaneous adsorption of molecules or formation of complex ions, (iv) finally, perfect reversibility exists in an exchange process under consideration.

On this basis, the Freundlich and Langmuir adsorption equations were proposed. The original form of the Freundlich

equation is

$$\frac{x}{m} = kC^{\frac{1}{p}}$$

where x is the amount adsorbed, m the weight of the material taken and C the equilibrium concentration of the electrolyte; K and 1/p are constants. Wiegner (72) used this equation in 1912. This equation has two weaknesses: (a) it does not flatten out at higher values of C, as a system with a fixed exchange capacity should, (b) it shows that the exchange varies with the variation of the total volume, whereas Wiegner showed that the position of equilibrium was independent of volume. Jenny however, in 1926 overcame the second objection by suggesting the equation:

$$\frac{x}{m} = k\frac{C^{\frac{1}{p}}}{a-C}$$

With the variable character of two constants incorporated in this equation, a good agreement is often obtained with experimental data over a limited range. However, Marshall (73) has shown that it was superior as regards K, but 1/p varied erratically. A similar type of equation to the Langmuir's, with only one constant was proposed by Vageler (74), but it could not account for the variability of equilibrium with volume.

The first use of the law of mass action in formulating ionic exchange as a completely reversible reaction was made by

Ganssen (75), Kerr (76) investigated specific mass action equations for uni-univalent and uni-bivalent exchangers. They were of the forms:

$$\frac{(\bar{X}) \cdot (Y^{+})}{(\bar{Y}) \cdot (X^{+})} = K_1 \; ; \qquad \frac{(\bar{X})^2 \cdot (Y^{+2})}{(\bar{Y}) \cdot (X^{+2})} = K_2$$

the bar indicates the ion in the exchanger phase.

The constants K_1 and K_2 are termed as selectivity coefficients. The ionic terms represent concentrations in equilibrium solutions. But owing to the lack of knowledge about the activities of the ionic species in the exchanger phase the equilibrium constant could only be evaluated qualitatively or empirically. Bauman (77) and Gregor (78) pointed out the difficulties in terms of swelling and volume change particularly of the resins. The model introduced by Gregor, although thermodynamically less well defined brings out clearly the physical action of the swelling pressure. A more rigorous application of the law of mass action has been made by Boyd and his co-workers (79) in which the "solid solution" idea of Vanselow (80) has been the basis on the assumption that the ion exchange is a "solid solution" process.

In the above formulations all the exchange sites were tacitly assumed to be of equal value. Doubts regarding this were first clearly expressed by Wiegner (81) and his co-workers.

In order to explain some of their experimental results they postulated the existence of loosely and firmly bound ions on the surface of the same exchange substance. Without the necessary information regarding the surface characteristics of the silicates which Wiegner used for his work he had to invoke the idea of the existence of micro pores, edges and cleavages.

Jenny (82) envisaged a kinetic condition on the surface and derived a mass action equation representing the exchange process of univalent ions. This idea was later developed by Davis (83) to multiply charged ions. Krishnamoorthy and Overstreet (84) applied the statistical method as has been used by Fowler (85) and Guggenheim (86) in the case of gas adsorption on solid surface. The attempts to understand ion exchange reactions on the basis of the electrical double layer, as postulated by Mukherjee (87) yields no doubt qualitative results but the concept in many respects, conforms better with observations. He assumed two categories of exchangeable ions, the osmotically active ions which constitute the mobile part of the double layer and the osmotically inactive ones constituting the immobile part of the double layer. The interpretation of the electrochemical properties of clays in terms of these two categories of ions has been in many ways very fruitful. The relationship of crystalline structure of clays, their electrochemical properties and ion-exchange characteristics have been studied with fundamental details by Mukherjee and Mitra (88),

Mitra and Bagchi (89), Ganguly and Mukherjee (90) and Chakravarti (91).

In the present thesis the exchange data obtained with bentonite, vermiculite, laponite, resin and molecular sieve and some inorganic and organic cations have been attempted to fit in the models like (i) Kielland's (92) and (ii) Pauley's (93).

Kielland's Model:

The first attempt to describe the ion-exchange equilibria by a theoretical equation which deviates from the regular pattern was made by Kielland. He introduced the use of solid phase activity coefficients and followed Vanselow (94) in treating the heteroionic form of ion exchanger as a solid solution of the components $\bar{A}$ and $\bar{B}$, the bars referring to the exchanger phase.

For the exchange of ions of any valency according to the reaction

$$m\bar{A}^{n+} + nB^{m+} \rightleftharpoons mA^{n+} + n\bar{B}^{m+}$$

Kielland's equation takes the general form as

$$\log K = \log K_a \quad C \left[n - 2n\bar{x}_B + (n-m)\,\bar{x}_B^2 \right]$$

where K = selectivity coefficient

K_a = thermodynamic equilibrium constant

$\bar{x}_B$ = equivalent ionic fractions of B in the exchanger phase

C = a constant.

Recently this equation has been given a sounder theoretical foundation by Barrer and Falconer (222). They derived the Kielland equation (92) by using statistical mechanical arguments for the special case when both the cations of the exchanging pair are univalent.

Pauley's model:

Pauley has interpreted selectivities in ion exchange equilibria in the language of a very simple model. Its essential feature is the electrostatic attraction between the counterions and the fixed ionic groups. It is assumed that all the counter ions in the ion-exchanger are found at their distance of closest approach to the fixed ionic groups. Writing AR and BR for the pairs of fixed ionic groups and counterions at the distance of closest approach, one can split the exchange of A for B into the two processes;

$$AR \longrightarrow A + R \qquad \ldots \qquad (1)$$

$$R + B \longrightarrow BR \qquad \ldots \qquad (2)$$

Coulomb's law (without any correction) leads to the following results for the above processes:

$$\Delta G_1^\circ = \int_{a_A^\circ}^{\infty} \frac{e^2}{r^2 \epsilon}\, dr = \frac{e^2}{a_A^\circ \epsilon} \qquad \ldots \quad \ldots \quad \ldots \quad (3)$$

and $$\Delta G_2^\circ = \int_{\infty}^{a_B^\circ} \frac{e^2}{r^2 \epsilon}\, dr = - \frac{e^2}{a_B^\circ \epsilon} \quad \ldots\ (4)$$

where ΔG_1° and ΔG_2° are the free energy changes for the processes (1) and (2); e = electronic charge; ϵ = dielectric constant; r = distance from center of fixed charge; a_i° = distance of closest approach between counter ion i and fixed ionic group. Hence the overall free energy change is

$$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ = \frac{e^2}{\epsilon}\left(\frac{1}{a_A^\circ} - \frac{1}{a_B^\circ}\right) \quad \ldots\ (5)$$

and the thermodynamic equilibrium constant K_A^B is

$$\ln K_A^B = - \frac{\Delta G^\circ}{kT} = \frac{e^2}{kT\epsilon}\left(\frac{1}{a_B^\circ} - \frac{1}{a_A^\circ}\right) \quad \ldots\ (6)$$

In the exchanges of various univalent counter ions i for an arbitrary univalent reference ion A, a linear relationship should exist between $\ln K_A^i$ and $1/a_i^\circ$. For multivalent ions, the calculation is not quite as simple because assumptions must be made as to how the (univalent) fixed ionic groups and the polyvalent counter ions are paired. The model leads qualitatively to preference of the ion exchanger for counter ion with smaller a° value and higher valency.

SECTION C

Exchange studies and Selectivities of Clay minerals, Resins and Molecular Sieves.

The exchange properties of clay minerals have been thoroughly investigated by a number of workers and their characteristics have been well established. The following generalisations may be made regarding the tendency of a cation to exchange onto a negative surface. There is an increase in exchangeability (a) with decreasing hydrated radius and increasing polarizability, (b) with decreasing ease of cation hydration and (c) with increasing counterion charge. The above criteria however, do not hold good in cases where some specific interactions take place. In accordance with the above observations, the order of increasing preference of alkali metal ions for ion exchange onto montmorillonite (33, 95-115), vermiculite (116) and kaolinite (117, 118) is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The exchange of ammonium ion is complicated by physical adsorption of ammonia (119) and fixation of ammonium ion (120). It was observed that ammonium ion is held more strongly than sodium ion (121) or even rubidium ion (122).

Similarly, the exchange of hydrogen ion is also complicated due to its attack onto the clay lattice, freeing aluminium

and magnesium ions which may be taken up by the exchange sites (123-130). It was reported that hydrogen ion is apparently preferred over some divalent cations in ion exchange on montmorillonite and clay soils (102, 131, 132), and over caesium on vermiculite (116). Several other investigations deal with the exchangeability of hydrogen ion on clay; the reported relative orders of exchange on montmorillonite are $H^+ < Cs^+$ (108), $K^+ < H^+ < Ca^{2+}$ (133), and $K^+ < NH_4^+ < H^+ < Mg^{2+}$ (33). Under conditions which minimise dissolution of clay by acid attack, the corresponding orders were $H^+ < Na^+ < K^+$ (99), and $Na^+ < H^+ < NH_4^+$ (121). The order of exchange of alkaline earth ions on clays has generally been reported as $Mg^{2+} < Mn^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (99, 102, 121, 134-144). The reverse order is sometimes found in vermiculite (141, 145, 146). The orders of exchange of divalent transition metal cations on clays reported are $Mn^{2+} \simeq Ni^{2+} \simeq Fe^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$ (147), $Ca^{2+} < Co(II)^{2+}$ (148) and $Ni^{2+} < Ba^{2+}$ (143). A generalisation may be made from studies comparing the exchange of mono, di and trivalent cations on clays that there is a preference for cations of higher charge (33, 98, 100, 102, 106, 107, 131, 133, 136, 140-142, 148-153), although there is exception to this trend.

The exchange of various alkyl ammonium cations from aquous solution by sodium laponite has been studied by Vansant and Peeters (154). They observed that the affinity of the clay

for these organic cations was linearly related to the molecular weight, molecular size or chain length of the alkyl ammonium ions. The affinity for the clay increases regularly with increasing chain length of the primary amines. Vansant and Yariv (155) have studied adsorption and oxidation of dimethyl aniline by laponite and the colour reaction mechanism was investigated.

In the usual general-purpose cation exchangers the selectivity sequence of the most common cations is (156-159):

$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+}$

$Tl^{+} > Ag^{+} > Cs^{+} > Rb^{+} > K^{+} > NH_4^{+} > Na^{+} > Li^{+}$.

The sequences of the univalent and bivalent cations overlap in resins of high capacity and moderate and high degree of cross linking. For strong acid resins, H^{+} usually falls between Na^{+} and Li^{+}. For weak-acid resins, the position of H^{+} depends on the acid strength of the fixed anionic groups.

The selective uptake of Li^{+}, Na^{+}, and K^{+} by a series of methacrylic acid cation-exchange resins of various divinyl benzene contents was measured by Gregor et al (160). The general order of preference was $Li^{+} > Na^{+} > K^{+}$. This preference became more marked as the degree of neutralisation of any given resin increased. This resin behaviour was compared by the authors with the association evidenced by the alkali metal acetates.

The ion-exchange properties of the synthetic zeolites X and Y have been investigated by a number of workers. Sherry (161) has determined exchange isotherms for a range of monovalent

inorganic cations in Na-X and Na-Y. His results have led to the conclusion that there is more extensive ion binding in Zeolite X as compared with the type Y which has a higher silica content and a lower exchange capacity. The effect of different silica- to - alumina ratios on cation selectivity has also been observed by Ames (162, 163) for a number of naturally occurring and synthetic zeolites. The crystal structure of zeolites X and Y encloses three different kinds of inter-connecting cavities in which the exchangeable cations are located on different crystallographic sites (164-166). Sherry (161) has interpreted his exchange isotherms in terms of the distribution of Na^+ ions over different crystallographic sites as revealed by the early x-ray studies of Broussard and Shoemaker (164) and summarised by Breck (166). Since the cavities are entered by windows of definite dimensions, steric and ion sieve effects have been observed in exchanges involving large cations (161,167). The intra crystalline space may be filled by these large cations before complete replacement of the ions initially present, is achieved. Hence, the extent of exchange may also be limited by the space requirement of the cations (167). Barrer et al (167), Theng (168) and Vansant et al (169) studied the exchange adsorption of ammonium and some of its alkyl derivatives in different natural and synthetic zeolites. They observed that for steric reasons, none of the alkyl ammonium ions could effect a complete replacement of the Na^+ ions initially present in the

zeolite so that the exchange reaction was confined to the large cavities in the crystal. The maximum extent of exchange decreased with an increase in molecular weight and polarizability of the cations but was always below the limit imposed by the space requirement of the respective ions. This decrease was also greater for the di- and tri alkyl derivatives than for the mono alkyl ammonium ions of comparable molecular weight and was more pronounced in X than in Y. The importance of affinity of the cations in determining the upper limit to exchange was further shown by the observation that for a given alkyl ammonium ion this limit decreased with an increase in the affinity of the inorganic ion which it replaced from the zeolite, the order being Li > Na > K > Ag > Tl (1). Vansant and Vanhoof (170) recently studied the exchange of alkane diammonium ions in the zeolites X and Y. They concluded that for steric reasons, none of the organic cations could effect a complete replacement of Na ions initially present in the zeolite. For any given alkane diammonium ion the maximum exchange capacity decreases with an increase in the affinity of the cations initially present in the zeolite, the order being $Li^+ > Na^+ > K^+$. Barrer (171), Sherry (161) and Cremers (172) described the exchange equilibria and selectivities of alkali, alkaline earth and rare earth ions for different zeolite ion exchangers. These results have led to the conclusion that there is more extensive ion binding in the X zeolite as compared with the Y type, which has a higher

silica content and a lower total exchange capacity. Barrer & Rees et al (173) have studied the thermo chemistry and thermodynamics of ion exchange with the Na ions in Linde Sieve X. They observed that from the determination of the standard free energy of exchange, ΔG^{o}, the following affinity sequence was established : $Li^{+} < Na^{+} < Ca^{2+}$, $K^{+} < Sr^{2+}$, $Cs^{+} < Ba^{2+} < Rb^{+}$.

The ion exchange behaviour of some transition metal ions in synthetic zeolite X and Y was studied by A.Maes et al (174) and they observed that the overall selectivity of both X and Y zeolite for bivalent transition metal ions increases in the order Ni < Co < Zn < Cu. In addition to the ion hydration characteristics and ionic radius the exchange is governed by the coordination ability of the transition metal ion.

Hence the more important characteristics of exchange studies are:

(i) the observation of the lyotropic series though exceptions are often observed.

(ii) obedience to the Langmuir equation of the data on exchange sorption of large organic molecules especially the dye molecules.

A simple equivalent fraction exchange equation has been proposed to fit in with the exchange data of Na^{+} , K^{+} and Ca^{2+} for Al^{3+} on bentonite (175) at 0.50 and 1.0(M) external salt concentration.

(iii) Formulation of selectivity coefficient. Exchange measurements can be written in a general way as follows:

$$\frac{1}{Z_1}\bar{A} + \frac{1}{Z_2}B \rightleftharpoons \frac{1}{Z_1}A + \frac{1}{Z_2}\bar{B}$$

(where the bar denotes the species in the clay phase and Z_1, Z_2, the valencies of A and B respectively), from which selectivity coefficient is expressed by the equation,

$$K_A^B = \frac{[A]^{\frac{1}{Z_1}}[\bar{B}]^{\frac{1}{Z_2}}}{[\bar{A}]^{\frac{1}{Z_1}}[B]^{\frac{1}{Z_2}}}$$

The selectivity coefficient measurements and obedience to the Langmuir equation are not, however, exclusive of one another.

All these studies are confined to the replacement of one inorganic cation for another. There is very little work on exchange reactions involving two organic cations.

Barrer (176) in a series of papers studied the exchange of one inorganic ion for organic ions. The sorption properties of montmorillonite was seen to change with the adsorption of quaternary ammonium ions $(CH_3)_4N$ and $(C_2H_5)_4N$. The tetramethyl ammonium or tetraethyl ammonium derivative of montmorillonite adsorbs an increased amount of oxygen at 78° and 90°K. Due to the adsorption of the quaternary ammonium ions the lamella of

the clay minerals are opened up and oxygen in increased amounts is adsorbed in the interlamellar space. McAtee (177) treated sodium bentonite with dimethyl benzyl lauryl ammonium (DMBL) ion. It was seen that almost 1:1 replacement of sodium took place upto 90 m.e/100 gm. of dry clay. The clay was thus converted into the DMBL form. This organic - clay derivative was taken in a suspension of a mixture of isopropyl alcohol and isooctane (20% isopropyl alcohol) and different amounts of dimethyl diocta decyl ammonium ion (DMDO) were added. The amounts of DMBL released was then measured using ultraviolet spectroscopy. It was seen that 16% of the DMBL cation was exchanged.