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 important role. Hence, a study of the exchange behaviour of clay fraction reveals, generally, the exchange characteristics 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. Only in this century, however, a systematic attempt has been made to understand the origin of their behaviour. But even then the surface chemistry of clay minerals has not been adequately investigated. Considerable success has been achieved in the past forty years in regard to the search for high purity clays and for evidences of their crystallinity. The atomic structure of the clay minerals has been to a great extent elucidated, and applied to explain the properties of the individual members.

The structures of some of the clay minerals used in the present investigation are briefly discussed, indicating their differences from each other and their pecularities, which are responsible for the special colloidal behaviour of the minerals. The clay minerals are classified into several groups such as kaolinite, montmorillonite, illite, chlorite and vermiculite. Mixed layer lattice type minerals have also been identified in natural clays.

The correlation between the structure of the clay minerals and their properties has been established as a result of the importan contributions of Pauling (1), Bragg (2), Gruner (3), Brindley (4), Hofmann (5), Marshall (6), Hendricks (7), Mauguin (8), Jackson (9), McMurchy (10), Barshad (11), Walker (12), Grim (13), MacEwan (14) and others. It is known that all the clay minerals consist essentially of two units. One is composed of two layers of closely packed oxygens or hydroxyls in the centre of which aluminium or magnesium ion is arranged in such a manner that the six oxygens or hydroxyls are in octahedral coordination with the metal ion.

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 bulk formula $Al_2(OH)_6$. When magnesium is present in octahedral coordination all the possible positions are filled giving the brucite structure having the bulk formula $Mg_3(OH)_6$.

The other unit is the tetrahedral silica layer. Silicon atom is placed in the cavity formed by four oxygen atoms such that the latter are in tetrahedral coordination with it. 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. 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 center 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 center 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.

An important phenomenon exhibited by clay minerals is their power of sorbing cations and retaining these in an exchangeable state. This can be explained by considering the existence of an unbalanced lattice charge of clay minerals, which makes them behave as colloidal electrolytes. 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.

Systematic studies of cation exchange in pure clay minerals were carried out by Page and Baver (17), Bar and Tenderloo (18), Hendricks and Alexander (19), Schachtschabel (20), Mukherjee (21) and others. They observed certain specificities in the exchange behaviour of the various clay minerals which were traced to their characteristic lattice configurations. Most of the earlier investigations on exchange equilibria, selectivity etc. were primarily based on the results of interaction of clays with simple inorganic (22-24) and organic cations (25,26) but very little study on the adsorption and desorption of inorganic trivalent complex cations has been reported so far. The physicochemical 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 is reviewed below.

Amongst earlier workers, Renold (27) (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. Jenny and Engabaly (28) (1943) showed, on the basis of the exchange characteristics of zincmontmorillonite that Zn ion is partially rendered non-exchangeable by being co-ordinated to the clay mineral. Basu and Mukherjee(29,30) 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 Glaeser (31) 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 (32) 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 trisethylenediamine cobaltic ion adsorbed on an ion exchange resin has been proposed for obtaining a high yield and specific activity (33). 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 trisethylenediamine cobalt (III) ion is suitable for this method, because these complex ions give rise to the bivalent cobaltous ion upon neutron irradiation (34-37). The retention of hexammine cobalt ion is, however, found to be lower than the corresponding value for the trisethylenediamine cobalt ion using the dynamic method (33). Chakravarti and Laitinen (38) studied sorption and desorption of $Coen_3Cl_3$ on Pyrex glass. The exchange capacity determined from the exchange of $[\overset{*}{Co}en_3]^{3+}$ agreed well with those obtained from the sorption and desorption studies of $\overset{*}{Cr}_{51}{}^{3+}$ and $\overset{*}{Cs}{}^{+}_{137}$. The recent studies on exchange characteristics of different aluminosilicates, viz., zeolites by Barrer (39) and others have also aroused considerable interest in this field. An interesting study, for instance, has been made of the exchange of different ions with Na^+ in a natural chabazite by Barrer *et.al.* (39). For the ions that exchange almost completely the thermodynamic affinity sequence, based on the standard free energies of exchange, is : $Tl > K > Ag > Rb > NH_4 > Pb^2 > Na = Ba^2 > Sr^2 > Ca^2 > Li$. All the ions except Cs^+ exchange completely with Na^+. Divalent ions, having greater charge/radius ratios than univalent ions of comparable radii, should be able to interact more strongly with the anionic sites, suggesting that one would observe a greater preference by the exchanger for the divalent ions. Obviously, since the affinities of Ca^{2+} and Ba^{2+} are not greater than those of Na^+ and K^+ respectively, Barrer *et al.*(loc.cit) concluded that other factors including the solvation affinities in the external solution must operate.

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 (40), Gieseking (41) and his colleagues (42,43) 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 early works of Hofmann et al.(44) and that of Myers (45) and Sharov (46) suggested that organic compounds with polar active groups could be adsorbed by clay minerals. Later, it was shown by Bradley (47,48) and MacEwan (49,50) that the non-ionic organic molecules of polar character could be adsorbed by the clay minerals. The work of Hendricks (51) and Grim et al.(52) also revealed that the organic ions are bound to the clay minerals by Van der Waals force in addition to coulombic force. Bradley and Grim (53) believe that the coulombic force is supplemented by C - H-- O bonds between the organic molecule and the clay mineral surface. It has also been shown by Grim et al. (52)that the sorption of organic cations will depend on the base exchange capacity of the clay minerals. Thorough investigations by other workers (54-56) have also been done 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 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 inorganic ions by a number of inorganic and organic cations.

Section B

Ion-exchange Formulations

Several approaches (57), both qualitative and quantitative, have been made to understand the equilibria between an ion-exchanger and ions in solution. Experiments were conducted in which concentrations of ions were varied, the result suggested an exponential relationship between ions adsorbed (or desorbed) and concentration of the exchanging ion. On this basis various formulations, e.g., similar to Freundlich and Langmuir's adsorption isotherm were proposed.

The mass action principle was also applied. 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 (58) and Gregor (59) 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 (60) in which the "solid solution" idea of Vanselow (61) 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 (62) 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 (63) envisaged a kinetic condition on the surface and derived a mass action equation representing theexchange process of univalent ions. This idea was later developed by Davis (64) to multiply charged ions. Krishnamoorthy and Overstreet (65) applied the statistical method as has been used by Fowler (66) and Guggenheim (67) 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 (68) 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 (69), Mitra and Bagchi (70), Ganguly and Mukherjee (71) and Chakravarti (72,73).

In the present thesis the exchange data obtained with bentonite, vermiculite and resin and some inorganic and organic cations have been similarly applied to several well known models, namely those of Barrer (74) & Pauley (75).

Barrer's model:- By the use of statistical thermodynamics, Barrer has derived an equation which is remarkably successful in describing the behaviour of most regular and irregular system with and without phase transition. The assumptions of Barrer are as follows:-

(1) When two entering ions, B, occupy adjacent crystal sites in the A-rich lattice, an additional change in the free energy of the crystal occurs.

(2) This change is negligible when ions A, B occupy adjacent sites relative to the state A, A ions occupy adjacent sites.

(3) The change in energy is additive with respect to the number of pair B, B independently of whether these pairs are in clusters or isolated.

(4) Apart from this energy change all other interactions between the energy change and the partition functions of ions A and B in the framework and of the frame work may be neglected.

(5) The distribution of ions on sites is assumed random.

(6) The amount of intracrystalline water is taken as unaltered by exchange.

In irregular systems in which accommodation of the larger ions becomes more and more difficult as conversion progresses, occupancy of two neighbouring sites by two large ions is evidently less favourable than occupancy by one large and one small or by two small ions. At constant overall ionic composition of the exchanger (Cf. zeolite), there is a characteristic difference in energy between the occupancy of two neighbouring sites by two ions B and by two ions A and B or two ions A. This energy may be written as 2 E_W/Z, where E_W is an(positive or negative) interaction energy and Z is the coordination number of the lattice. A statistical distribution of the exchange sites occupied by two ions B is assumed. The number of these pairs is $Z\bar{n}_B/2\ \bar{n}_Z$ ($\bar{n}_B$ = number of counter ions B in the zeolite; $\bar{n}_Z$ = number of exchange sites).

In this way a simple expression giving the total partition function of the zeolite can be obtained. By differentiation of this expression and use of the equilibrium condition, the following relation is obtained:

$$\ln \frac{\bar{n}_A\ a_B}{\bar{n}_B\ a_A} = \ln \frac{\bar{J}_A(T)}{\bar{J}_B(T)} + \frac{\mu^0_A - \mu^0_B}{RT} + \frac{\bar{E}_A - \bar{E}_B}{RT} + \frac{2\ \bar{n}_B}{\bar{n}_Z} \cdot \frac{E_W}{RT} \text{------} (1)$$

where $\bar{J}_i$ = partition function of the species i in the zeolite;

$\bar{E}_i$ = energy of the species i in the zeolite;

μ_i° = standard chemical potential of species i.

After substituting equivalent ionic fractions $\bar{x}_i = \bar{n}_i/(\bar{n}_A + \bar{n}_B)$, one obtains

$$\ln K_B^A = \ln \frac{\bar{x}_A \, a_B}{\bar{x}_B \, a_A} = \ln \mathcal{K}_B^A + C(1 - 2\bar{x}_B) \text{ -------}(2)$$

The quantity $\mathcal{K}_B^A$ is the rational thermodynamic equilibrium constant and K_B^A is the corrected selectivity coefficient. So that a plot of ln K_B^A against $(1 - 2\,\bar{x}_B)$ should give a straight line, the intercept being equal to ln $\mathcal{K}_B^A$ and slope is equal to C.
Comparison with equation (1) shows that

$$\ln \mathcal{K}_B^A = \ln \frac{\bar{J}_A(T)}{\bar{J}_B(T)} + \frac{\mu_A^\circ - \mu_B^\circ}{RT} + \frac{\bar{E}_A - \bar{E}_B}{RT} + \frac{(\bar{n}_A + \bar{n}_B)}{\bar{n}_Z} \frac{E_W}{RT} = \text{constant}$$

and that the constant C is

$$C = - \frac{\bar{n}_A + \bar{n}_B}{\bar{n}_Z} \frac{E_W}{kT}$$

The second term on the right hand side of eqn. (2) arises from the gain or loss in free energy resulting from interaction between the neighbouring sites occupied by ions B. In "regular" systems this term is zero since no interaction occurs. In irregular systems in which occupancy of two neighbouring sites by two ions B is unfavourable, the constant C is negative.

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 counter ions 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 counter ions at the distance of closest approach, one can split the exchange of A for B into the two processes:

$$AR \longrightarrow A + R \quad \ldots\ldots \quad (3)$$

$$R + B \longrightarrow BR \quad \ldots\ldots \quad (4)$$

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

$$\Delta G_1^\circ = \int_{a_A^\circ}^{\infty} \frac{e^2}{r^2 \epsilon}\, dr = \frac{e^2}{a_A^\circ \epsilon} \quad ----- (5)$$

and

$$\Delta G_2^\circ = \int_{\infty}^{a_B^\circ} \frac{e^2}{r^2 \epsilon}\, dr = -\frac{e^2}{a_B^\circ \epsilon} \quad ---- (6)$$

where ΔG_1^0 and ΔG_2^0 are the free energy changes for the processes (3) and (4); e = electronic charge; ϵ = dielectric constant; r = distance from center of fixed charge; a_i^0 = distance of closest approach between counter ion i and fixed ionic group. Hence the overall free energy change is

$$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ = \frac{e^2}{\epsilon}\left(\frac{1}{a_A^\circ} - \frac{1}{a_B^\circ}\right) \quad ------ (7)$$

and the thermodynamic equilibrium constant K_A^B is

$$\ln K_A^B = -\frac{\Delta G^0}{RT} = \frac{e^2}{kT\epsilon}\left(\frac{1}{a_B^0} - \frac{1}{a_A^0}\right) \text{-------} (8)$$

Therefore, a linear relationship should exist between $\ln K_A^i$ and $\frac{1}{a_i^0}$. The model leads qualitatively to preference of the ion exchanger for counter ion with the smaller a^0 value and counter ion of higher valency.

Section C

Exchange studies and Selectivities of Clay minerals and Resins.

The exchange properties of clay minerals have been thoroughly studied by a number of workers and their characteristics have been well established. The more important characteristics are:

(i) the observation of the lyotropic series (76) though exceptions are often observed.

Hofmann (77) studied the activities of Na , K , NH_4 , Ca , Mg , Ba as exchangeable ions on clay minerals. The effect of exchangeable ions on the sorptive properties of palygorskite and halloysite (78) was studied to give the sorptive properties ranking more or less in the order : $Mg^{2+} \gg Ca^{2+} > Fe^{3+} > H^{+} > Al^{3+} > Na^{+} > K^{+}$ for both the clay minerals. Displacement of Zn^{2+} , Cu^{2+} , Mn^{2+} , Co^{2+} and Ni^{2+} by H_2SO_4 and H-Resin (79) gave the order $Zn^{2+} > Mn^{2+} > Ni^{2+} \gg Co^{2+} > Cu^{2+}$ for both acid and the H-resin but the amount desorbed was greater with the acid.

In another study (80) a relation between Ni^{2+} and Co^{2+} released from Ni-H-clay, Co-H-clay and the pH of the solution was observed. The lyotropic series was also noticed for sorption of each of the quaternary ammonium ions NMe_4, NEt_4 , NPr_4 and NBu_4 against Li^{+} , Na^{+} , H^{+} , NH_4^{+} and K^{+}(81). The exchange of methylene blue with respect to H^{+}, Ca^{2+} and K^{+} on bentonite, illite and kaolinite (82) was found to be in the order : $H^{+} > Ca^{2+} > K^{+}$ and for the clays the order is : illite > bentonite > kaolinite.

The exchange reaction between Ca^{2+} and Mg^{2+} was observed to be unusual (83) and it was proposed by Beckett (84) that except for certain specific spots Ca^{2+} and Mg^{2+} have got equal sorption affinities.

In the usual general purpose cation exchangers the selective sequence of the most common cations is (85-88) :
$Ba > Pb > Sr > Ca > Ni > Cd > Cu > Co > Zn > Mg > UO_2 > Tl > Ag > Cs >$
$Rb > K > NH_4 > Na > Li$.

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 ionic 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. (89). The general order of preference was $Li^+ > Na^+ > K^+$. This preference became more marked as the degree of neutralization of any given resin increased. This resin behaviour was compared by the authors with the association evidenced by the alkali metal acetates.

(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 (90) 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,

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

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 (91) 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 and oxygen in increased amounts is adsorbed in the interlamellar space. McAtee (92) treated sodium bentonite with dimethyllauryl-benzylammonium ion (DMBL). It was seen that almost 1:1 replacement of sodium took place upto 90 me/100 gm dry clay. The clay was thus converted into the DMBL form . This organo - clay derivative was taken in a suspension of a mixture of isopropyl alcohol and isooctane (20% isopropyl alcohol) and different amounts of dimethyldioctadecylammonium ion (DMDO) were added. The amounts of DMBL released was then measured using ultraviolet spectroscopy . It was seen that 16% of the DMBL ion was removed by DMDO .