CHAPTER - I

SECTION - A

Introduction and Review of previous work:

The process of ion exchange is the mechanism operative during uptake of ions by plant roots from clay minerals and other soil components. In this process the clay fraction of the soil plays a significant and vital role. The study of the exchange characteristics reflects 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. The contribution of our knowledge of clay minerals is largely due to scientists, colloid Chemists, Ceramicists and physicists who have appreciated in their respective fields the importance of the clay minerals. A systematic attempt has however been made only in this century to understand the origin of their behaviour. Considerable success has been achieved in the past fifty years with 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.

In general clay means a natural fine-grained earthy material which develops plasticity when mixed with a limited quantity of water (1). Clay is basically the product of weathering of rocks or of hydrothermal action. It is also used in terms of particle size. In that case it is defined as a material having particle size lower than 2.0 microns. The material below 2.0 micron is primarily the colloidal product of weathering and hence constitutes the active portion of the soil (2,3,4). The fraction is mainly composed of clay minerals but may sometimes be associated with non clay mineral substances.

The composition and crystalline structure of clay minerals are now well established with the help of such techniques as X-ray, electron diffraction, differential thermal analysis, electron microscopy and other optical studies (4) besides chemical, electrochemical, ion-exchange and viscous properties.

The clay minerals have been classified under separate headings, such as kaolinite, montmorillonite, illite, chlorite and vermiculites. Mixed layer lattice type minerals have also been identified in natural clays.

On the basis of crystal chemical approach, the correlation between the structures and the exchange properties of the clay minerals has been established from the important researches of Pauling (5), Bragg (6), Gruner (7), Brindley (8), Hoffmann (9), Marshall (10), Hendricks (11) and others (12-18). 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 co-ordination 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 up to balance the structure giving that of brucite which has the formula $Mg_3(OH)_6$. The second unit is the tetrahedrally co-ordinates silica. A silicon atom being placed at the centre of a regular 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. The structures for some of the alumino-silicates used in the present study are described briefly.

Kaolinite:

The kaolinite is composed of a single silica tetrahedral together with a single alumina octahedral sheet confined 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 the 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 tetrahedra are, pointed in the same direction and toward the centre of the unit. The tetrahedral and the octahedral sheets are combined in such a way 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 the 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 into the space between the sheets causing expansion of the axis in the c-direction.

Isomorphous substitution of other metal ions for silicon and 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.

Laponite:

Laponite is a synthetic clay of the hectorite variety. Hectorite is a natural mineral swelling clay and usually remains heavily contaminated with other minerals such as dolomite, quartz etc which are not easily removed. The deposits of hectorite are also limited. Laponite provides for the first time, a reliable consistent supply of high purity swelling clay. It has a number of other important properties not found in its natural equivalent. It is composed of magnesium silicates with a layer structure and is obtained as granular, free-flowing white powder. The powder forms thixotropic gels when dispersed in water. Laponite has a layer structure similar to that of the natural hectorite. Hectorite is the trioctahedral equivalent of montmorillonite and owes its charge to octahedral replacements of Mg by Li.

Its structural formula is

$$[\,\mathrm{Si}_8\,]^{IV} \quad [\,\mathrm{Mg}_{6-x}\cdot \underset{\substack{\downarrow \\ M_x}}{\mathrm{Li}_x}\,]^{VI} \quad O_{20}(OH)_4$$

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

$$\mathrm{Na}_{0.70}(\mathrm{Mg}_{5.26},\ \mathrm{Li}_{0.59})\ \mathrm{Si}_{0.01}O_{24}H_{3.97}$$

In certain Laponite products, there are no fluorine atoms in the structure, these are being replaced by hydroxyl ions. The layers (platelets) are about 10Å thick and are extended in two dimensions. If the cations present were only 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.

Usually during crystal growth, the tetrahedra are not solely occupied by silicon or by aluminium or magnesium. Aluminium may substitute for some of the tetrahedral silicon atoms and Fe, Li, Mn, Cr and other metal ions of suitable size may occupy a part of the octahedral sites. This isomorphous replacement of ions unbalances the overall charge of the crystal lattice. An excess negative charge develops which is balanced by cations that are retained on the external layer silicate surfaces. These cations, e.g. Na^+, K^+, Ca^{2+} and others are more or less exchangeable, depending on the nature of the replacing cations, nature of the adsorbed cations and the magnitude and distribution of the structural charge. They are held between unit layers and bond the layers together. This brings the idea of cation exchange capacity (C.E.C.) of the clay.

The ion exchange sorption of inorganic as well as organic ions is known to occur in clay minerals (19,20). Hence the origins of the charge of the clay lattice are believed to be due to isomorphous 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 counter ions are held on the external surfaces of the aggregates and between the unit layers in clays which swell in aqueous suspension, whereas the sorption of counter ions takes place onto the external surfaces only in non-swelling clays. In aqueous suspension, some of these cations remain in a closely held stern layer, others diffuse away from the surface and thus 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 counter ions can undergo ion exchange with other cations present in the system.

The magnitude of the C.E.C. 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 differ from sample to sample, and the nature of the counter ions present in the sample may also 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 (21), Bar and Tenderloo (22), Hendricks and Alexander (23), Schachtschabel (24), Mukherjee (25) and others. Most of these investigations were based upon exchange equilibria, selectivity etc. with simple inorganic ions (26,27). Exchange reactions involving clay minerals with organic compounds have also been established by different scientists (28-31).

Amongst earlier workers, Renold (32) 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 exchangibility of these cations in the order shown. Zn was found by him to be as effective as Ba in its exchanging power. Jenny and Elgabaly (33) showed, on the basis of exchange characteristics of Zn montmorillonite that Zn ion is partially rendered non-exchangeable by being coordinated to the clay mineral. Basu and Mukherjee (34-35) have studied in detail the interaction of montmorillonite clay and trace element cations. Thev 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 (36) studied the adsorption of $Co(NH_3)_6Cl_3$ on montmorillonite under various pH conditions. They found that it also permits the estimation of internal and external exchange capacities. Chakravarti and Laitinen (37) studied the adsorption and desorption of $Coen_3Cl_3$ on pyrex glass. The exchange capacity determined from the exchange of $[Coen_3]^{3+}$ agreed well with those obtained from the sorption and desorption studies of Cr^{3+}_{51} and Cs^{+}_{137}. Das Kanungo, Chakravarti and Mukherjee (38, 39,40) studied adsorption and desorption of hexamine Cobalt (III) chloride and trisethylene diamine Cobalt (III) chloride on bentonite and vermiculite and observed that adsorption is according to Langmuir's equation and desorbing cations arrange themselves according to the lyotrope series. Recently, Sarkar and Das Kanungo (41) have shown that in the exchange of tri-strimethylene diamine Co (III) from the bentonite matrix by alkaline earth metal ions, both the hydrated ionic radius and the reciprocal of the Debye-Huckel ion-size parameter, a^o, may be used to correlate the relative affinities of the ions for the mineral while for the alkali metal ions only, $1/a^o$ may be utilised for the purpose. Thielmann and McAtee, Jr. (42) 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) Co(III) and Na^+ on montmorillonite was studied by Knudson, Jr. and McAtee, Jr. (43) and concluded that the exchange of $Co(en)_3^{3+}$ for Na^+ was extremely favourable, with a tendency towards segregation of the two kinds of cations in the mixed clays studied. The studies on exchange characteristics of Zeolite, either synthetic or natural by Barrer and his co-workers (44) and others have received a great deal of attention in recent years.

Interlayer complexes of clays with simple organic compounds are essentially of two types, those in which the adsorbed species exists (a) as a cation and (b) as a polar non-ionic compound. From a study of the reactions between organic compounds and different type of clays made by a large number of workers, the specific nature of the clay mineral organic ion reactions has now been fairly well established. Under suitable conditions, most organic cations are capable of replacing the interlayer inorganic cations occupying exchange sites in montmorillonite and vermiculite type minerals.

Hendricks (45) extended Gieseking's (46) study of organic bases, cations and proteins on montmorillonite to other aliphatic and aromatic amines, alkaloids, purines and nucleosides using H-montmorillonite as adsorbent. He was able to show that small organic bases neutralised the H^+ ions upto or close to the exchange capacity of montmorillonite as determined by the exchange with Ba^{2+}. On the other hand, large alkaloids, such as brucine and codeine, failed to neutralise all the H^+ ions present in the clay. This led Hendricks to postulate that the difference between the total amount of H^+ ions and that available for reacting with the alkaloid represents the quantity "covered" by the organic base. This cover-up-effect comes into operation when the size of the adsorbed organic molecules exceeds the area per exchange site. of the complexes formed in this way, those involving n-alkylammonium ions received the greatest amount of attention. The chemistry of clay-organic reactions has been well reviewed by Greenland (47), Mortland (48) and Theng (49). A number of general conclusions has emerged from these studies by Hendricks (45), Jordan (50), Cowan and White (51), Diamond and Kinter (52), Weiss (53), Theng et al (54), Walker (55), Vansant and Uytterheoven (56), Maes et al (57) and others and is summarized below:

(1) Adsorption reaches a maximum equal or close to the exchange capacity of the clay. For very long chain derivatives

($>C_8$), adsorption may exceed this capacity, the excess being present as the free amine.

(2) For montmorillonite, the affinity of the organic ion for the clay, increases regularly with molecular weight, that is, the larger the cation, the stronger its adsorption. This observation is ascribed to the increased contribution of van der Waals forces to the adsorption energy as the molecular weight increases and also to the changes of the hydration status of the ions in the clay interlayer.

(3) Basal spacing measurements suggest that the organic ion is adsorbed with its shortest axis perpendicular to the silicate layer, since such a flat conformation enables close van der Waals contact to be achieved between the adsorbate and substrate.

(4) Single-layer complexes [$d_{001} \simeq 12.5-13.5$ Å] are formed with montmorillonite provided that the area of the cation (upto C_{10}) is less than the area per exchange site since the organic ions adsorbed on one layer can fit into the gaps between those adsorbed on the opposing surface. If, however, the cation area ($>C_{10}$) exceeds the area per exchange position, this lock-and-key arrangement is no longer possible and double layer complexes [$d_{001} \sim 16.5 - 17.5$ Å] are obtained.

(5) At high surface concentrations, long-chain alkylammonium ions ($>C_{10}$) may assume an "end-on" orientation in which

the alkyl chain extends away from and makes a definite angle with the silicate surface. In this conformation greater van der Waals interactions between alkyl chains are possible. The interlayer space is also increased so that a larger amount of the organic ions can be accommodated.

(6) In vermiculites the tilted conformation is generally observed even for short-chain derivatives since the distance of separation of the negative charges in the silicate surface is less than for montmorillonite. The basal spacing of vermiculite complexes tends to show a continuous rather than a step-wise increase with the number of carbon atoms in the alkyl-chain. Double layer complexes of vermiculite have been observed at high solute concentrations.

(7) There is evidence to indicate that partially exchanged montmorillonite crystals are composed of "inorganic ion rich" and "alkyl ammonium rich" layers as shown by Barrer and Brummer (58), Theng et al (54) and others.

Sorption studies of dyes and large organic ions on different adsorbents, particularly on clays, have been made by innumerable workers over a period of many years. Most of the earlier studies have been confined to the measurement of the surface areas and c.e.c. of the adsorbents. Relevant literature is reviewed in the following paragraphs.

As early as 1910 Mare (59) observed that dyes could be adsorbed by crystals upto a saturation value. Ramachandran et al (60) measured the surface area by low temperature nitrogen adsorption before and after adsorption of methylene blue, methyl violet and malachite green on the clay fraction of kaolinite, illite and montmorillonite. From the difference, the actual extent of the area of contact was evaluated. This was found to be relatively small showing that while the surface is available for nitrogen adsorption, it is not accessible to dye molecules. The cation exchange capacities, found from methylene blue and methyl violet sorption on kaolinite and montmorillonite, were in close agreement with those found by standard methods.

Brooks (61) adsorbed methylene blue on Na^+ forms (Na^{22} and Na^{23}) of kaolinite, montmorillonite and found the amount of dye adsorbed to be equivalent to the sodium displaced; he believed that the dyes were adsorbed, at the first stage, on the clay mineral surface through ion-exchange process. More dye is adsorbed after that, which was explained to be due to van der Waals forces. Plesch and Robertson (62) also proposed two distinct mechanisms to operate in the sorptions of dyes on surfaces of clay minerals viz. the partly irreversible ion-exchange and the fully reversible physical adsorption. Bergmann and O'Konski (63) reported that the adsorption of methylene blue on montmorillonite took place first through irreversible ion exchange mechanism and then by physical adsorption and verified the equation of Plesch and Robertson with their experimental results.

From the studies of adsorption of crystal violet on anatase and rutile and that of orange II on anatase, rutile and zinc oxide, Ewing and Liu (64) estimated the cross-sectional areas of crystal violet and orange II. They assumed that the dye molecules were adsorbed flat on the surface and accordingly they estimated the cross-sectional area of crystal violet to be 160 $\mathring{A}$ and 171 $\mathring{A}^2$ depending on whether the dye is adsorbed in the dehydrated or hydrated condition. The area occupied by one orange II molecule was calculated to be 140 $\mathring{A}^2$. The surface areas of the adsorbents, calculated on the basis of these cross-sections, were in excellent agreement with those found out by low temperature nitrogen gas adsorption and also by electron microscopic analysis. Clauss, Rohem and Hofmann (65) reported 78 $\mathring{A}^2$ as the cross-sectional areas of methylene blue from the adsorption data on graphitised and non-graphitised carbon. The value of 130 $\mathring{A}^2$, for a flat molecular orientation, agreed excellently with that observed by Loss and Tompkins (66) and Langville et al (67). Surface areas of calcined magnesia, alumina, silica and silica gel were calculated from methyl red adsorption (68). The results were reported to agree within 6%.

An agreement was also noticed in the values of surface areas calculated from the adsorption of monosulphonated acid wool dye (sodium salt of 1-amino, 4-anilino, anthraquinone, 2-sulfonic acid) from aqueous solution and that from nitrogen adsorption. An N-H...O bond between the dye and the adsorbate was suggested (69).

The surface areas measured through dye adsorption, however, did not agree with those obtained by nitrogen adsorption in all cases. Kipling and Wilson (70) found discrepancies in specific surface areas of porous and non-porous active charcoal measured by methylene blue and nitrogen adsorptions. Hofmann (71), on the basis of methylene blue and orange II adsorption on a wide variety of clays, showed that the surface area calculated was only 70% of the total surface area. Orr (72,73) found that the surface areas of two halloysite samples calculated by sorption of four dyes viz. malachite green oxalate, malachite green hydrochloride, amaranth and tetrazine, were apparently equal to one-fourth of the total surface. Similar discrepancies were also reported by Darau (74), van der Grinter (75) and Bancellin (76) in their respective adsorption studies, viz., ethyl violet on silica, crystal violet on glass and methylene blue on mercury. Bancroff et al (77) from adsorption of methylene blue on lead sulphate, Subrahmanya et al (78) from crystal violet adsorption on glass and Doss and Singh (79) from thymol blue sorption on active carbon, arrived at similar unsatisfactory results.

Giles et al (80) observed that the adsorption of basic dyes by silica from aqueous solution exceeded its monolayer coverage requirement. They opined that the dyes were adsorbed on the surface not as a single unit but as ionic micelles. This was confirmed by the adsorption of methylene blue and pseudocyanine chloride by spectroscopic examination of the solution before and after adsorption. Association of the dye molecules in the adsorbed state has also been detected directly by electron micrography (81). That most of the dye molecules are associated in solution as micelles from 10 to 100 molecular units was reported by Lenhar and Smith (82,83), Vickerstaff and Lenin (84) and Bergmann and O'Konski (63). Mukherjee and Ghosh (85, 86,87) and Hertz et al (88) and Hertz (89) also observed that dye molecules, of which the monovalent organo cations are a sub-group, tend to aggregate into dimeric and polymeric species in aqueous solution. Kongonovoski (90) also viewed the adsorption of dyes to take place through monolayer sorption of associated micelles.

Brooks (61), however, advocated that the surface area and cation exchange capacity of the substrates, with methylene blue adsorption, could still be measured. To calculate the c.e.c. and surface areas, he suggested addition of dye solution to a mineral suspension in small increments till the equilibrium concentration was 1×10^{-6} (M), indicated by a slight blue colour of the supernatant.

Hang Pham Thi and Brindley (91) asserted that methylene blue can be used for the measurement of both surface areas and c.e.c. of clay minerals such as kaolinite, illite and montmorillonite. They attributed the cause of failures in measuring surface areas and exchange capacities by Faruki et al (92) and Bodenheimer and Heller (93) to the insufficient replacement of Ca^{2+} ions by methylene blue from Ca-montmorillonite used in their studies. Using Na-clay instead of the Ca-clay these authors calculated surface areas from the amount of methylene blue adsorbed when optimum flouculation occurred. Fully exchanged values of methylene blue was used to calculate the c.e.c. of the montmorillonite. Methylene blue molecule was considered to possess approximately a rectangular volume of dimensions 17.0 x 7.6 x 3.25 $\mathring{A}^3$. They believed that coating of clay particles occurred first and visualised a flat face-on orientation of methylene blue molecules (i.e. lying on the 17.0 x 7.6 $\mathring{A}^2$ face for effective coverage of surfaces. Flat side-on orientation of the dye (i.e. 17.0 x 3.25 $\mathring{A}^2$ face)was assumed when full exchange took place. Brindley and Thompson (93a) later extended this work to montmorillonite saturated with different cations and obtained expected values of the surface areas and c.e.c.

West, Carrol and Whitcomb (94) investigated systematically the adsorption characteristics of more than thirty dyes on photographic bromo-iodides or chloro-bromides suspension in 70% aqueous gelatine solution in an attempt to correlate the sorption and optical sensitisation. It was noticed in some cases that the dye adsorbed was very little at first but the rate of increase of dye adsorption increased as more dye was adsorbed. They termed this as 'co-operative adsorption'. The intermolecular forces between the large dye molecules are so high that they polymerised when the molecules came closer in the adsorbed state, giving rise to increased rate of adsorption.

De et al (95-104) made a series of exhaustive studies on sorption of dyes on to clay minerals and on their desorption from the clay-dye complexes by various inorganic and organic ions. They found Langmuir type of adsorption isotherms to operate in all cases. Surface area measurement, evaluation of c.e.c., determination selectivity coefficients and distribution coefficients are the highlights of their work. Narine and Guy (105) interacted thionine, methylene blue, New Methylene blue, paraquat and diquat with bentonite in dilute aqueous systems. They noted that the dye cations form aggregates on the clay surface and aggregation increases with ionic strength, raising the apparent adsorption capacity by 25%. The aggregates were, however, removable by washing with distilled water. They also observed that changes in adsorption due to changes in temperature were small and the dyes were irreversibly bound by the clay matrix.

Yamagashi (106) recently studied the effect of alkyl chain length ($-CH_3$ to $-C_{14}H_{29}$) for the adsorption of n-alkylated acridine orange cations on Na-montmorillonite. He observed that the length of the aliphatic tail had no appreciable effect on the binding constant of adsorption, the rate of adsorption and the angle of the transition moment due to a bound dye with respect to electric field but the 'mobility' of a bound dye to an empty site of another colloidal particle was remarkably affected by the alkyl chain. Two factors, viz. steric hindrance and hydrophobic interactions among the alkyl chains of adjacent sorbed dye molecules, were supposed to influence the mobility of bound dye in opposite ways. This finding demonstrates the ability of a clay to recognise the shape of a molecule and strengthens the possibility of using clay as shape-sensitive catalyst (107). Mishra et al (108) studied the sorption behaviour of two basic dyes, brilliant cresyl blue and Safranine-T, on chemically pretreated hydrous tin (IV) oxide under varying surface phase pH, concentration, temperature and desorbents. Reed and Rogers (109) observed selective adsorption of methyl and ethyl orange on tailored silica gel.

So, it appears from the review above that the sorption of cationic dyes, although believed to be primarily an ion exchange process, is rather complicated by many other factors such as molecular size, molecular geometry, dye-dye interaction, besides, of course, the surface characteristics of the sorbents. Our knowledge of the physico-chemical aspects of the desorption processes of the organic dye cations from the clay surfaces 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 behaviours of Rhodamine B and Rhodamine 6G. On and from montmorillonite, kaolinite, laponite and monovalent, bivalent inorganic ions and organic ions of varying size and shape and also an approach has been made to study comparative adsorption behaviour between Rhodamine B and Rhodamine 6G with Brilliant cresyl blue on different aluminosilicates.

SECTION - B

Ion Exchange Formulations

A number of approaches, both qualitative and quantitative, have been made to understand the equilibria between an ion exchanger and the ions in solution (1). A review of cation exchange equations as they are being used in soils and in other exchnagers has been done by Bolt (2) and Helfferich (3) and their applicability to soils discussed by Babcock (4). Experiments were performed in which the ionic concentrations were varied and the result suggested an exponential relationship between the ions adsorbed (or desorbed) and the concentration of the exchanging ions. Limitations have been tacitly accepted in most mathematical treatments of exchange reactions.

Thus (A) the simultaneous occurrence of both cation and anion exchange reactions in a given system has been considered as a rare case, (B) the exchange capacity to be constant, though cases are known where the exchange capacity varies markedly with the change in pH and the nature of the exchanging ion, (C) simple stoichiometric equivalence between the ions taken up and released is generally assumed to be present, deviations are usually explained in terms of simultaneous adsorption and formation of complex ions, and (D) finally the perfect reversibility exists in an exchange process under consideration.

On this basis, various formulations similar to Fruendlich and Langmuir's adsorption equations (isotherms) were proposed. The Fruendlich equation is emperical and can be expressed as where 'X' is the amount of adsorbate taken up by 'm' gm of

$$\frac{X}{m} = k.\ C^{1/n}$$

adsorbent, 'k' and 'n' are constants and 'C' is the adsorbate concentration in solution at equilibrium.

Weigner (5) used this equation in 1912. But this equation has two limitations, (i) it does not flatten out at higher values of 'C' as a system of fixed exchange capacity should, and (ii) it shows that the exchange varies with variation of total volume, whereas Weigner (5) showed that the position of equilibrium was independent of volume. Weigner and Jenny (6), however, in 1927, overcome the second objection and modified the equation as

$$\frac{X}{m} = K \left(\frac{C}{a-c} \right)^{1/n}$$

[a = initial concentration of the adsorbate].

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 and Gupta (7), has shown that it was superior as regards 'k' but $\frac{1}{n}$ varied erratically.

The Langmuir isotherm is based on sound kinetic and thermodynamic principles and was developed to describe the adsorption of gases onto solids. It assumes that only monomolecular adsorption takes place, that adsorption is on localised sites, that there are no interactions between adsorbate molecules and that the heat of adsorption is independent of surface coverage When V is the equilibrium volume of the gas adsorbed per unit mass of adsorbent at pressure P, then

$$V = \frac{V_m \cdot K.P}{1 + KP}$$

where K is a constant dependent on temperature, and V_m is the volume of the gas required to give monolayer coverage of unit mass of adsorbent. When applied to adsorption from solution, this equation takes the form (8)

$$\frac{X}{m} = \frac{(x/m)_{max} \cdot K.C}{1 + K.C}$$

where 'X' is the amount of the solute adsorbed by mass 'm' of adsorbent, 'C' is the equilibrium solution concentration, 'K' is a constant, and $(\frac{X}{m_{max}})$ is the monolayer capacity.

By use of the reciprocal expression, the above equation becomes,

$$\frac{1}{(X/m)} = \frac{1}{K.\ (X/m)_{max}} \quad \frac{1}{C} + \frac{1}{(X/m)_{max}}$$

So a plot of 1/x/m versus 1/C should give a straight line and a slope of $\frac{1}{K(X/m)_{max}}$ when the Langmuir relationship holds good.

A similar type of equation of the Langmuir's with two constants were proposed by Vageler (9,10) as

$$X = \frac{Sa}{a + C}$$

where X = amount exchange, a = electrolyte added

S and C = constants.

Application of the Langmuir's adsorption equation to cation exchange in soils was initiated by Vageler (9) in 1932. His equation appears to be an erroneous attempt to restate the Langmuir equation in terms of amounts of the cation added to the system rather than its concentration at equilibrium. It may be shown that only when the ratio of the forward and backward rate constants is close to unity such a restatement is acceptable and in all other cases it does not appear to be sound (11).

Aside from Vageler's equation, the original Langmuir equation is in its simplest form useless for cation exchange, as it does not take into consideration the competition between the cationic species. One may, however, introduce this competition effect into the Langmuir equation rather simply by using Kerr's (12) and Gapon's (13) equations as a starting point (2). However, should an ion-exchange mechanism predominate in the adsorption process, the linear forms of the Langmuir and Fruendlich equations would not be obeyed because of coulombic effects in the adsorbent. Thus, in theory at least, it is possible to distinguish by means of different isotherm equations between ionic and other mechanisms of adsorption (14).

The ion exchange formulations are usually based on three theories i.e. (i) crystal lattice theory (ii) double layer theory and (iii) Donan membrance theory (15). The only differences in the various theories are the position and the origin of exchange sites. In all cases, this site is essentially a fixed, non-diffusible ionic grouping capable of forming an electrostatic bond with a small diffusible ion of opposite charge. The case with which this latter ion may be replaced depends on the strenth of the bond, which varies in a manner similar to the dissociation of weak and strong electrolytes. The laws governing the exchange of ions in these heterogeneous systems are analogous to the laws governing the solutions of electrolytes.

Jenny (16) envisaged a kinetic condition on the surface and derived from statistical approach the equation below,

$$W = \frac{+(S+N) \pm \sqrt{(S+N)^2 - 4SN\left(1 - \frac{\nu_w}{\nu_b}\right)}}{2\left(1 - \frac{\nu_w}{\nu_b}\right)}$$

where W = number of cations exchanged at equilibrium

N = number of cations added initially

S = saturation capacity

and W,b = constants for each ion.

For similar exchange properties of the two exchanging ions, the above equation reduces to

$$W = \frac{SN}{S + N}$$

which is quite similar to that of Vageler (9,10).

A more refined approach was introduced by Davis (17,18) and applied to exchange on soil clays by Krishnamoorty and Overstreet (19). Davis considered the probability of replacement of cations with different valency on a regular array of negative point charges as supposed to be present on the exchanger surface. Although, Davis, indicates that his treatment should apply to a monolayer in the widest sense of the word in each surface charge is being accompanied by one counter charge only in the adsorbed layer, it appears that other assumptions inherent in the treatment as, e.g., absence of anions, probability of replacement being based on a regular array of the position available for the ions, are warranted only if one considers a monolayer in a narrow sense, i.e. localized monolayer.

The first use of the law of mass action in formulating ion exchange as a completely reversible reaction was made by Gansen (20) and Kerr (12), investigating specific mass action equations for uni-univalent and uni-bivalent exchanges as

$$\bar{Y} + X^{+} \rightleftharpoons Y^{+} + \bar{X} \qquad 2\bar{Y} + X^{2+} \rightleftharpoons \bar{X} + 2Y^{+}$$

$$K_1 = \frac{[\bar{X}][Y^{+}]}{[\bar{Y}][X^{+}]} \qquad K_2 = \frac{[\bar{X}][Y^{+}]^2}{[\bar{Y}]^2[X^{2+}]}$$

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 equilibrium concentration in solution. 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 emperically. Bauman (21) and Gregor (22) pointed out the difficulties in terms of swelling and volume change particularly of the resins. The model introduced by Gregor (22) although thermodynamically less well-established, bring 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 co-workers (23) in which the "solid solution" idea of Vanselow (24) has been the basis on the assumption that the ion exchange is a "solid solution" process. Vanselow visualizing the monolayer as an ideal two dimensional solid solution, assumes the activities of the two exchanger components to be proportional to their respective mole-fractions.

In the above formulations, all the exchange sites were assumed to be of equal value. Doubts regarding this, were first clearly expressed by Weigner (25) and his co-workers. In order to explain some of their experimental data, they postulated the existence of loosely and firmly bound ions on the surface of the same exchanger. Without the necessary information regarding the surface characteristics of the silicates which Weigner used for this work, he had to invoke, the idea of the existence of micropores, edges and cleavages. A remark should be made here on the assumed reversibility of the exchange reaction. There is evidence that certain exchange reactions are incompletely reversible. The obvious example of such a system is the adsorption of potassium by certain clay minerals. There steric factors influence the relative affinity of the clay for different cations, which necessitates the recognition of a range of sites with different relative affinity (26,27). The fact that often the cationic composition in turn influences these steric factors (by a varying degree of collapse of the crystal lattice) suggests a considerable degree of hysteresis in exchange reaction involving inter-lattice sites.

Attempts to understand ion exchange reactions on the basis of electrical double layer, as postulated by Mukherjee (28) 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 osmotically inactive ones constituting the immobile part of the double layer. The relationship of crystalline structure of clays with their electrochemical properties and ion exchange characteristics has been studied with fundamental details by Mukherjee and Mitra (29), Mitra and Bagchi (30), Ganguli and Mukherjee (31) and Chakravarti (32).

However, in a more detailed study of the exchange behaviour of soil materials, the monolayer model equations do not offer much perspective for interpretative usage. One should then rather use, the thermodynamic method of presentation as suggested by Gaines and Thomas (33,34). The most promising model for the description of adsorption on external surfaces appears, however, to be a Stern-Gouy double layer approach along with lines as used for the homovalent case by Heald et al (35) and further advanced by Shainberg and Kemper (36,37). Extension of this model to heterovalent exchange will increase its complexity considerably, as both the fraction of the multivalent ions in the Gouy layer and that in the Stern layer will depend on the valency. The contribution of Shainberg and Kemper (36,37) is of great interest as an effect to estimate the magnitude of the pair - formation constants on the basis of the physical properties of the ions and presents an important stepforward in the process of gaining understanding about the nature of the cation exchange equilibrium in clay systems.

Considerable progress has also been made by others (38, 39,40) in the formulation of ion exchange equilibria on a rigorous and quantitative basis. Further progress must await new advances in the fields of concentrated solutions of simple electrolytes and soluble, uncrosslinked polyelectrolyte solutions which has been stepped by Fuoss (41), Katchaesky (42) and others.

In the present thesis an attempt has been made to fit the adsorption data of two xanthene dyes viz. Rhodamine B and Rhodamine 6G and one oxyazine dye viz. Brilliant Cresyl blue on montmorillonite, kaolinite and laponite in the Langmuir equation and the desorption data of the two xanthene dye cations from their respective adsorbent complexes by monovalent and bivalent inorganic ions in the model of Pauley (43).

Pauley's Model:

Pauley has interpreted selectivities in ion exchange equilibrium 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 two processes:

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

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

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

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

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

where ΔG_1^o and ΔG_2^o are the free energy charges for the processes (1) and (2), e = electronic charge, ϵ = dielectric constant, r = distance from the centre of the fixed charge, a_i^o = distance of the closest approach between counter ion 'i' and fixed ionic group. Hence the overall free energy change for the whole process is

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

and the thermodynamic equilibrium constant K_A^B is

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

In the exchange of various univalent counterions 'i' for an arbitrary univalent reference ion A, a linear relationship should exist between In K_A^B and $\frac{1}{a_i^o}$.

For multivalent ions, the calculation is not quite as simple because assumptions must be made as to how the (univalent) fixed ionic groups and polyvalent counterions are paired. The model leads qualitatively to preference of the ion exchanger for counterion with smaller a^o value and higher valency.

SECTION - C

Exchange studies and Selectivities of Clay minerals

A true ion-exchange equilibrium is completely reversible and may be approached from both sides of the reaction equilibrium provided that certain conditions are observed. These conditions are determined by the selectivity of the ion exchanger which in turn is influenced by Donnan effects, specific interactions, steric effects, ion association and other ion-sequestering effects (1). Where these effects are large the equilibrium will favour one side of the reaction. Specific interactions and Donnan effects largely determine ion selectivity in most situations. Specific interactions (e.g. hydrogen bonding, van der Waals forces, charge-transfer processes, etc.) can produce secondary adsorption interactions on the counterion bound by the exchanger. These increase the selectivity of the adsorbent for the adsorbed ion, and this ion is then held preferentially despite the presence of high concentrations of counterions in solution (2,3,4). Steric effects can also influence reversibility, as evidenced in ion trapping effects. In some systems ion-sequestering effects (including ion-pairing, complexing and precipitation) are important in determining selectivity. Generally, the adsorbent prefers the ion which associates least strongly in solution and most strongly with the adsorbent (4). A number of workers have thoroughly investigated the exchange properties of the clay minerals, resins and molecular sieves 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 ionic radius and increasing polarizability, (b) with decreasing case 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 (5-26), vermiculite (27) and kaolinite (28,29) is $Li^+ \angle Na^+ \angle K^+ \angle Rb^+ \angle Cs^+$. The exchange of NH_4^+ is complicated by physical adsorption of ammonia (30) and fixation of NH_4^+ ion (31). It was observed that NH_4^+ is held strongly than Na^+ (32) or even Rb^+ (33).

Similarly the exchange of H^+ is also complicated due to its attack onto clay lattice, displacing aluminium or magnesium ions which may be taken up by the exchange sites (34,35). It was reported that H^+ is apparently preferred over some divalent cations in ion exchange on montmorillonite and soil-clays (13,36) and over caesium on vermiculite (27). The reported relative orders of exchange on montmorillonite are $H^+ \angle Cs^+$ (16), $K^+ \angle H^+ \angle Ca^{2+}$ (7) and $K^+ \angle NH_4^+ \angle H^+ \angle Mg^{2+}$ (37). Under conditions which minimise dissolution of clay by acid attack, the corresponding orders were $H^+ < Na^+ < K^+$ (10) and $Na^+ < H^+ < NH_4^+$ (32). The sequence of exchange of alkaline earth ions on clays has generally been reported as $Mg^{2+} < Mn^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (10,13,32,38-48), The reverse order is sometime found in vermiculite (45,49,50). For the exchange of divalent transition metal cations on clays, the reported orders of preference are $Mn^{2+} \simeq Ni^{2+} \simeq Fe^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$ (51) $Ca^{2+} < Co(II)^{2+}$ (52) and $Ni^{2+} < Ba^{2+}$ (47). 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 (37,7,11,13,16,17,36,40,44-46,52-57) although there is exception to this trend. In the usual general purpose cation exchangers, the selectivity sequence of the most common cations is $Ba^{2+} \geq Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > mg^{2+} > Uo_2^{2+} > Tl^+ > Ag^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+$ (58-61).

Under suitable conditions, most organic cations are capable of replacing the interlayer inorganic cations, occupying exchange sites in bentonite, vermiculite and illite minerals.

The exchange reaction is stoicheiometric except for some bulky cations when a cover-up effect (62) may operate. Studies on the replacement of exchangeable sodium and calcium from montmorillonite by various alkyl ammonium cations were made by Theng et al (63). They found that the affinity of the clay for the organic cations was linearly related to molecular weight with the exception of the smaller methyl ammonium and larger quaternary ammonium ions. Thus, the more the length of the alkyl ammonium chain increases, the greater is the contribution of physical, non-coulombic forces to adsorption. Within a group of primary, secondary and tertiary amines, the affinity of the alkyl ammonium ions for the clay decreased in the series $R_3NH^+ > R_2NH_2^+ > RNH_3^+$. These differences were explained in terms of size and shape of the ions. Theng et al also noted that Na^+ was much more easily exchanged bv the alkyl ammonium ions than was Ca^{2+}. In studies in which the alkyl ammonium ion is replaced by metal cations, Mortland and Barake (64) showed that the order of effectiveness in replacing ethylammonium ion was $Al^{3+} > Ca^{2+} > Li^{2+}$. Furthermore, X-ray diffraction studies on partially exchanged systems revealed that the organic and inorganic cations were not distributed uniformly throughout all the surfaces of montmorillonite, but that a segregation of the two kinds of ions took place in various layers. This suggests that when the displacement of ethylammonium ion by the metal ion from one interlamellar position begings, it is completed before ethylammonium ions from other layers are exchanged. Similar observations have been reported by Barrer and Brummer (65), McBride and Mortland (66) and Theng et al (63). The exchange of various alkylammonium cations from aqueous solution by Na-Laponite has been carried out by Vansant and Peeters (67). They observed that the affinity of these organic cations was linearly related to molecular weight, molecular size or chain length of the alkylammonium ions. The affinity sequence has been attributed to the increasing contribution of van der Waals force to adsorption energy as the size of the ions increases (68) and also to the change in hydration state of the ions in the clay interlayer (69,70).

Charge density of the clay mineral may also affect the orientation of adsorbed organic cations through steric effects. Thus, Serratosa (71) showed by infra red absorption technique that in pyridinium montmorillonite, the organic cation assumed an orientation where the plane of the pyridine ring was parallel with the platelets of the clay mineral and a resulting d_{001} spacing of 12.5 $\overset{o}{A}$. On the other hand, pyridinium-vermiculite has the pyridinium cations vertically positioned with respect to the clay platelets and a d_{001} spacing of 13.8 $\overset{o}{A}$. Apparently, the close proximity of the cation exchange sites one to another prevents the pyridinium ring from assuming the parallel position because of the restricted area permitted for each pyridinium unit. When neutral but polar organic molecules are bound to the clay surface by other mechanisms, such as ion-dipole interaction, charge density would also be expected to affect their orientation within the interlamellar regions of swelling clay minerals. It is apparent from the review above that 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 observations 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 (specially the dye molecules). A simple equivalent fraction exchange equation has been proposed to fit in the exchange data of Na^+, K^+, Ca^{2+} on bentonite (72) at 0.5(M) 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 in the adsorbed phase and Z_1, Z_2 and the valencies of A and B respectively.

From the above equation, the selectivity coefficient is expressed as follows:

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

The measurement of selectivity coefficient and the obedience of Langmuir's 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. The exchange of a large organic cation for another organic cation on montmorillonite had been reported by McAtee (73). Since the organo-montmorillonite is organophilic and hydrophobic, the exchange was carried out in an isooctane isopropyl alcohol mixture. It was found that under the condition of the experiment upto 16 per cent of dimethylbenzyllauryl ammonium cation can be replaced from montmorillonite with dimethyldioctadecyl ammonium cation. De, Das Kanungo and Chakravarti (74-77) have shown that cationic dyes e.g. methylene blue, crystal violet, and malachite green adsorbed onto bentonite, vermiculite, kaolinite and asbestos can be exchanged by long-chain surface active ions like cetyltrimethyl ammonium and cetyl pyridinium ions. In the present work, desorption of two xanthene dyes viz. Rhodamine B and Rhodamine 6G has also been studied with tetraalkyl ammonium and long-chain surface active ions of varying size and shape.