CHAPTER - I

SECTION - A

Introduction and Review of Previous Work:

Though investigation of clay minerals may be traced far back into antiquity, the clay mineral concept developed only in the present century with the systematic studies for the origin of the colloidal properties of clay mineral. 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 determined to a great extent and applied to explain the properties of the individual members by numerous investigators.

Correlation between the structures and the exchange properties of clay minerals has been established from the important research contributions of Pauling (1), Bragg (2), Gruner (3), Brindley (4), Hoffman (5), Marshall (6), Hendricks (7) and others (8-14). 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 the 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 then 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 with 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 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 clay minerals, used in the present investigation, are discussed briefly by way of introduction. Their differences from each other and their peculiarities responsible for the special colloidal behaviour have also been indicated.

Kaolinite : The kaolinite is composed of a single silica tetrahedral sheet and a single aluminium 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-directions. 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 and as a result of which very little expansion is possible in the c-direction.

Montmorillonite : According to the currently accepted concept, montmorillonite is composed of units made of two silica tetrahedra sheets with a central aluminium octahedral sheet. All the tips of the tetrahedra point in the same direction and towards the centre of the unit. The tetrahedral and 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 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 placed close to the O layers of the other unit with 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 by iron and magnesium is found in the minerals nontronite and saponite respectively. Substitution in the tetrahedral layer in montmorillonite takes place only to a limited extent.

<u>Vermiculite</u> : Alternate stacking of mica and water layers represents the vermiculite structure. 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 resultant 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+} ions 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 : 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 deposite 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 similar to natural hectorite and is obtained as a granular, free-flowing white powder. The powder forms thixotropic gels when dispersed in water. Hectorite is the trioctahedral equivalent of montmorillonite and owes its charge to octahedral replacements of Mg by Li. Its structural formula is

$$\left[Si_8\right]^{IV}\left[Mg_{6-x}\cdot\underset{\underset{Mg}{\downarrow}}{Li_x}\right]^{VI}\cdot\ O_{20}(OH)_4$$

The charge is of the order of 0.6 to 0.7 valencies per unit cell.

The structural formula of Na-Laponite CP is :

$$Na_{0.70}(Mg_{5.26},\ Li_{0.59})Si_{0.01},\ O_{24}H_{3.97}$$

In certain Laponite products there are no flourine atoms in the structure, these being replaced by hydroxyl ions. The layers are about 10 Å thick and are extended into two dimensions. If the cations present were only silicon and magnesium a single layer could 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. 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 bind the layers together. This gives rise to the idea of cation exchange capacity (c.e.c) of the clay mineral, which means the total number of exchangeable cations that the mineral can retain per 100 g.

Ion exchange sorption of inorganic as well as organic ions is known to occur in clay minerals (15 - 19). The origins of charge of the clay lattice are believed to be due to lattice imperfections, broken bonds at the edges of the particles and exposed structural hydroxyls in addition to the isomorphic substitution already mentioned. The negative charge on the clay minerals is compensated by adsorption of cations. The counter ions are held on the xternal surfaces of the aggregates and between the unit layers in clays which swell in aqueous suspension, whereas they are sorbed only onto the external surfaces in the non-swelling clays. In aqueous suspensions 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 being engaged in a strong, specific bonding with the clay or 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 mineral depends largely on the type of clay and to a lesser extent on the source of a particular sample.

Besides c.e.c., the specific surface area of a clay mineral is another important property that depends on the type of clay and also on the method of measurement employed. Among clays of the same type, the values differ from sample to sample; the nature of the counter ions present in the same sample may also influence the measured surface area. The theoretical surface areas are 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 (20), Bar and Tenderloo (21), Hendricks and Alexander (22), Schachtschabel (23), Mukherjee (24) and others. Most of these investigations were based upon exchange equilibria, selectivity etc. with simple inorganic ions (25,26). Exchange reactions involving clay minerals with organic compounds have also been established by different scientists (27-30).

Amongst earlier workers, Renold (31) (1930) was perhaps the first to study systematically the exchange behaviour of Cu, Pb, Ni, Ag, Zn, Hg and Cd permutite 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 Elgabaly (32)(1943) showed, on the basis of exchange characteristics of Zn-montmorillonite that Zn ion is partially rendered non-exchangeable by being co-ordinated to the clay mineral. Basu and Mukherjee (33, 34) 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 mineral surface by H^+. Moreover, quantitative measurement 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 (35) 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. Das Kanungo, Chakravarti and Mukherjee (37-39) studied adsorption and desorption of hexamine 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 desorbing cations arrange themselves into the lyotropic series. Recently, Sarkar and Das Kanungo (40) have shown that in the exchange of tris-trimethylene 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. The cation exchange process between tris (ethylene diamine) Co(III) and Na^{+} on montmorillonite was studied by Knudson, Jr. and McAtee, Jr. (42) and concluded that the exchange of $Co(en)_{3}^{3+}$ for Na^{+} was extremely favourable, with a tendency toward 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 (43) 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; in one type the adsorbed species exists as a cation and in the other as a polar non-ionic compound. 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 in montmorillonite and vermiculite type of minerals.

Following up the work on clay mineral-organic complexes that began as early as 1916, Gieseking and coworkers (29,36,41,45) examined the interaction of montmorillonite clays with a number of organic bases, cations and proteins. Hendricks (44) extended this study to other aliphatic and aromatic amines, alkaloids, purines and nucleosides using H-montmorillonite as adsorbent. He showed that small organic bases neutralised the H^+ ions up or close to the exchange capacity of the 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-alkyl ammonium ions received the greatest attention. The chemistry of clay-organic reactions has been well reviewed by Greenland (46), Mortland (47) and Theng (48). A number of general conclusions has emerged from these studies by Hendricks (44), Jordan (49), Cowan and White (50), Diamond and Kinter (51), Weiss (52), Greenland (46), Theng et al (53), Walker (54), Vansant and Uytterhoeven (55), Maes et al (56) and others and is summarised 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 free molecules.

(ii) For montmorillonite the affinity of the organic ion for the clay surface increases regularly with molecular weight, that is, the larger the cation, the stronger is its adsorption. This 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 in the hydration status of the ions in the clay interlayer.

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

(iv) Single-layer complexes ($d_{001} \simeq 12.5-13.5$ A$^{\circ}$) 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 ($d_{001} \simeq 16.5-17.5$ A$^{\circ}$) are obtained.

(v) 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.

(vi) 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 stepwise increase with the number of carbon atoms in the alkyl chain. Double-layer complexes of vermiculite have been observed at high solute concentrations.

(vii) There is evidence to indicate that partially exchanged montmorillonite crystals are composed of 'inorganic ion rich' and 'alkylammonium ion rich' layers as shown by Barrer and Brummer (57) and Theng et al (53) 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 Marc (58) observed that dyes could be adsorbed by crystals up to a saturation value. Ramachandran et al (59) 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 (60) adsorbed methylene blue on Na^{+} forms (Na^{22} and Na^{23}) of kaolinite, montmorillonite and silica sand flour 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 (61) 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 (62) 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 (63) 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 $\mathring{A}^2$ 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, Rohen and Hofmann (64) reported 78 $\mathring{A}^2$ and 130 $\mathring{A}^2$ 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 Ross and Tompkins (65) and Langille et al (66). Surface areas of calcined magnesia, alumina, silica and silica gel were calculated from methyl red adsorption (67). 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 (68).

The surface areas measured through dye adsorption, however, did not agree with those obtained by nitrogen adsorption in all cases. Kipling and Wilson (69) found discrepancies in specific surface areas of porous and non-porous active charcoal measured by methylene blue and nitrogen adsorptions. Hofmann (70), 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 (71, 72) 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 (73), van der Grinter (74) and Bancellin (75) in their respective adsorption studies, viz., ethyl violet on silica, crystal violet on glass and methylene blue on mercury. Bancroff et al (76) from adsorption of methylene blue on lead sulphate, Subrahmanya et al (77) from crystal violet adsorption on glass and Dose and Singh (78) from thymol blue sorption on active carbon, arrived at similar unsatisfactory results.

Giles et al (79) 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 (80). That most of the dye molecules are associated in solution as micelles from 10 to 100 molecular units was reported by Lenhar and Smith (81, 82), Vickerstaff and Lenin (83) and Bergmann and O'Konsi (82). Mukherjee and Ghosh (83a, 84, 85), Hertz et al (84) and Hertz (86) 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. Kongonovski (88) also viewed the adsorption of dyes to take place through monolayer sorption of associated micelles.

Brooks (60), 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 (89) 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 (90) and Bodenheimer and Heller (91) 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 flocculation 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 Å^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 Å^2 face) for effective coverage of surfaces. Flat side-on orientation of the dye (i.e. 17.0 x 3.25 Å^2 face) was assumed when full exchange took place. Brindley and Thompson (91a) later extended this work to montmorillonit saturated with different cations and obtained expected values of of the surface areas and c.e.c.

West, Carrol and Whitcomb (92) 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 (93 - 102) 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 of selectivity coefficients and distribution coefficients are the highlights of their work. Marine and Guy (103) 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.

Yamagoshi (104) 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 (105).

Dyes have also been adsorbed on non-clay materials and similar observation as in the case of clay minerals have been made. Mishra et al (106) studied the sorption behaviour of two basic dyes, brilliant cresyl blue and Safranine-T, on chemically pre-treated hydrous tin (IV) oxide under varying surface phase pH, concentration, temperature and desorbents. The sorption was found to be pH dependent and predominant ion-exchange behaviour was assumed.

Reed and Rogers (107) observed selective adsorption of methyl and ethyl orange on tailored silica gel. Either methyl or ethyl orange can be selectively adsorbed in increased amounts on silica gel by precipitating it in presence of methyl or ethyl orange.

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, that it can hardly be generalised for other exchange reactions. Though the adsorption characteristics of cationic dyes on different clay minerals have been investigated from various angles, similar studies on Laponite (a synthetic trioctahedral hectorite) are still lacking. The desorption characteristics of the dye cations from the clay-matrices have also not been very systematically studied with different inorganic and organic cations of varying size, shape and charge. Our knowledge of the physicochemical 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 behaviour of thionine and tetramethyl thionine on and from montmorillonite, vermiculite, Laponite and kaolinite by monovalent, bivalent and trivalent inorganic and organic ions of varying size and shape.

SECTION - B

Ion Exchange Formulations

A review of cation-exchange equations as they are being used in soil science has been done by Bolt (1) and their applicability to soils discussed by Babcock (2). Several approaches, both quantitative and qualitative, have been made to understand the equilibria between an ion exchanger and the ions in solution (3). Various formulations similar to Freundlich and Langmuir's equations (isotherms) were proposed. The Freundlich equation, which is empirical, can be expressed as :

$$x/m = K.c^{1/n}$$

where 'x' is the amount of adsorbate taken up by 'm' gm of adsorbent, 'K' and 'n' are constants and 'c' is the adsorbate concentration in solution at equilibrium. 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. Weigner and Jenny (4) modified the equation eliminating the volume term as :

$$x/m = K \frac{c}{a - c}^{1/n}$$

(a = initial concentration of the adsorbate).

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, 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

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

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 (5) :

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

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 $(x/m)_{max}$ is the monolayer capacity. Using reciprocal form the above equation becomes,

$$\frac{1}{(x/m)} = \left[\frac{1}{K. (x/m)_{max}} \right] . \frac{1}{C} + \frac{1}{(x/m)_{max}}$$

A plot of $1/(x/m)$ against $1/c$ should be a straight line with a slope of $1/K(x/m)_{max}$ when the Langmuir relationship holds good.

An equation with two constants similar to Langmuir's was proposed by Vageler (6,7) as :

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

where x = amount exchanged, a = electrolyte added and S and C are both constants.

Application of the Langmuir's adsorption equation to cation exchange in soils was initiated by Vageler (6) 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 (1).

Aside from Vageler's equation, the original Langmuir equation in its simplest form is useless for cation exchange as it does not take the competition between cationic species into consideration. One may, nevertheless, introduce this competition effect into the Langmuir's equation rather simply by using Kerr's (8) and Gapon's (9) equations as a starting point (1). However, should an ion-exchange mechanism predominate in the adsorption process the linear forms of the Langmuir and Freundlich equations will not be obeyed because of coulombic effects in the adsorbent. Thus, in theory at least, it is possible to distinguish between ionic and other mechanisms of adsorptions by means of different isotherm equations (10).

The ion-exchange formulations are usually based on three theories : (i) crystal lattice theory, (ii) double layer theory and (iii) Donan membrane theory (11). The only differences in the various theories are the position and origin of the exchange sites. In all cases, this site is essentially a fixed non-diffusible ionic grouping capable of forming an electrostatic bond with a small diffusable ion of opposite charge. The ease with which this latter ion may be replaced depends on the strength 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.

The first use of the law of mass action in formulating ion exchange as a completely reversible reaction was made by Gansen (19) and Kerr (8), investigating specific mass action equations for uni-univalent and uni-bivalent exchanges as :

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

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

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 concentrations in solution. Lacking information about the activities of the ionic species in the exchanger phase, the equilibrium constants could only be evaluated qualitatively or emperically. A more rigorous application of the law of mass action has been made by Boyd and his co-workers (13) in which the 'solid solution' idea of Vanselow (14) 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 present thesis an attempt has been made to fit the adsorption data of two thiazine dyes viz., Thionine and Tetra-Ethyl Thionine (TET) on montmorillonite, vermiculite, kaolinite and laponite in the Langmuir equation and the desorption data of the two dye cations from their respective adsorbent complexes by monovalent and bivalent inorganic ions in the model of Pauley (15).

Pauley's Model:

Pauley has interpreted selectivities in ion exchange equilibria by a very simple model. The essential feature of the model 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, the exchange of A for B can be split 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 formulations for the above processes :

$$\Delta G_1^0 = \int_{a_A^0}^{\infty} \frac{e^2}{r^2 . \epsilon} . dr = \frac{e^2}{a_A^0 . \epsilon} \qquad \ldots (3)$$

$$\Delta G_2^0 = \int_{\infty}^{a_B^0} \frac{e^2}{r^2 . \epsilon} . dr = - \frac{e^2}{a_\beta^0 . \epsilon} \qquad \ldots (4)$$

where ΔG_1^0 and ΔG_2^0 are the free energy changes for the processes (1) and (2), e = electronic charge, ϵ = dielectric constant, r = distance from the centre of the fixed charge, a^0 = distance of the closest approach between the counter ion 'i' and fixed ionic group. Hence the overall free energy change for the whole process is :

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0 = \frac{e^2}{\epsilon} \left(\frac{1}{a_A^0} - \frac{1}{a_\beta^0} \right) \qquad \ldots (5)$$

and the thermodynamic equilibrium constant K_A^B is :

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

In the exchanges of various univalent counter ions 'i' for an arbitrary univalent reference ion A, a linear relationship should exist between $\ln K_A^B$ and $1/a_i^o$. For the multivalent ions, the calculation is not 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 counterion with smaller a^o values 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 the selectivity. Generally, the adsorbent prefers the ion which associates least strongly in solution and most strongly with the adsorbent (4). 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 polarisability, (b) with decreasing ease of cation hydration, and (c) with increasing counter-ion charge. These 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 $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. 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 more 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 clay soils (13,36) and over caesium on vermiculite (27). The reported relative orders of exchange on montmorillonite are $H^+ < Cs^+$ (16), $K^+ < H^+ < Ca^{2+}$ (7) and $K^+ < NH_4^+ < H^+ < Mg^{2+}$ (37). Under conditions which minimise dissolution of clay by acid attack, the corresponding orders are $H^+ < Na^+ < K^+$ (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 sometimes 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 $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+} > Tl^+ > Ag^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+$ (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 stoichiometric except for some bulky cations when a cover-up effect (62) may operate. Studies on replacement of exchangeable sodium and calcium from montmorillonite by various alkylammonium cations were made by Theng et al (63). They found that the affinity of the clay for the organic cation was linearly related to molecular weight with the exception of the smaller methylammonium and large quaternary ammonium ions. Thus, the more the length of the alkylammonium 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 alkylammonium ions for the clay decreased in the series $R_3NH^+ > R_2NH_2^+ > RNH_3^+$. The differences were explained in terms of size and shape of the ions. Theng et al also noted that Na^+ was much more easily exchanged by the alkylammonium ions than was Ca^{2+}. In studies where the alkylammonium ion is replaced by metal cations, Mortland and Barake (64) showed that the order of effectiveness in replacing ethylammonium ion was $Al^{3+} > Ca^{2+} > Na^{+}$. Furthermore, X-ray diffraction studies on partially exchanged systems revealed that the organic and inorganic cations were not uniformly distributed 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 begins, 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 forces 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 infrared absorption technique that in pyridinium-montmorillonite the organic cation assumed an orientation where the plane of the pyridine ring was parallel with the clay platelets with a resulting d_{001} spacing of 12.5 A°. On the other hand, pyridinium-vermiculite has the pyridinium cations vertically positioned with respect to the clay platelets and has a d_{001}

spacing of 13.8 A°. Apparently, the close proximity of the cation exchange sites prevents the pyridinium ring from assuming the parallel position because of the restricted area available for each pyridinium cation. Where 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 observation of the lyotropic series though exceptions are often observed.

(ii) Obedience of Langmuir equation by 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 the exchange 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 measurement can be written in a general way as :

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

where the bar denotes the species in the adsorbed phase and Z_1, Z_2 are the valencies of A and B respectively from which the 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.

These studies are mostly 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 large organic cations by another cation on montmorillonite had been reported by McAtee, Jr. (73). Since the organo-montmorillonite is organophilic and hydrophobic, the exchange was carried out in an iso-octane-iso-propyl alcohol mixture. It was found that under the condition of the experiment, up to 16 per cent of dimethylbenzyllaurylammonium 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 montmorillonite, vermiculite, kaolinite and asbestos can be exchanged by long-chain surface active ions like cetyltrimethylammonium and cetylpyridinium ions. In the present work, desorption of two thiazine dyes viz., Thionine and Tetra-Ethyl Thionine (TET) has been studied with tetraalkylammonium, alkane di-ammonium and long-chain surface active ions of varying size and shape.