CHAPTER - I

SECTION - A

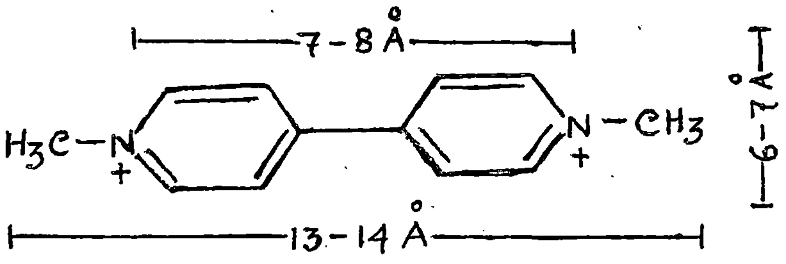
Introduction and Review of Previous Work

In to-day's ecologically-oriented society and also in agricultural and horticultural practice, there is a strong interest in all aspects of herbicide and pesticide use. The performance, mobility, persistence and residual problems of a herbicide applied to a soil are related directly or indirectly to the processes of its adsorption and desorption. Detailed physico chemical studies on the interactions of herbicides with soil constituents such as clay minerals and organic matter (1) can give an insight into the actual mode of action of such biologically active compounds and their ultimate fate in the soil environment. So a study of the processes of adsorption and desorption of a herbicide by soil clays, provides useful information with regard to its fate in the soil and reveals, generally, the exchange characteristics of the soil as a whole.

The herbicidal properties of Paraquat, (1,1'-dimethyl-4, 4'-bipyridylium dichloride), one of the most important bipyridylium herbicides, were discovered at ICI's Jealott's Hill Research Station, England, in 1955, although paraquat salts had been known since 1882 (2) and had been used as oxidation-reduction indicators under the name methyl viologen since 1932(3).

"Gramoxone" is the trade mark of Plant Protection Ltd., I.C.I, England for this bipyridylium herbicide. The properties of paraquat have been reviewed by Calderbank (4) and Akhavein and Linscott (5) and Summers (6). Paraquat is a broad spectrum, rapidly acting contact herbicide which is highly effective against grasses and most broad leaved species. It is effective as herbicide at low concentrations of about 0.14 - 2.2 kg/hectare. A unique property of paraquat is its rapid and complete adsorption onto soil. Paraquat that reaches the soil is rendered unavailable to plant roots and have no residual activity. It is used to kill emerged weeds anytime before planting a crop or before the crop emerges. Consequently, paraquat is widely used in Agriculture for preplant and pre-emergence weed control and it has an important use in minimum tillage farming systems. It is also used for weed control between trees and as a directed spray in row crops. Due to its desiccating properties, it finds wide application as a harvest aid.

The dimensions of paraquat estimated from its molecular model by Weed and Weber (7) are given below



Assuming that the cationic charge is associated with the nitrogen atoms, the charges on the paraquat are separated by about 7-8 A^o and the extreme dimensions of the cation are 13-14 A^o and 6-7 A^o in length and thickness respectively. In this compound the two pyridylium rings are coplanar and the ability to adopt a planar configuration appears to be necessary for herbicidal activity.

Burdon, Hayes and Pick (8) have recently calculated the charge distribution of paraquat by a Complete Neglect of Differential Overlap semi-emperical quantum mechanical procedure. The electron density data, however, show that the positive charges in the organo cation are distributed around the molecule and are greatest in the positions *ortho* and *para* to the heterocyclic nitrogen atoms. Earlier interpretations of the mechanism of adsorption of paraquat by soils and clays, however, assumed that the charges are located in the hetrocyclic nitrogen atoms.

Paraquat is highly soluble in water and dissociates to give divalent organic cation. It is a non volatile compound (9) and is stable in acid and neutral solutions but decomposes above pH 12 (4). Paraquat adsorbed on glass slides or thin layers of soil is photochemically degraded in sunlight or under UV lamps (4). However, photochemical degradation of significant amounts on soil surfaces in the field has not been clearly demonstrated. The herbicide exhibits strong absorption in the ultraviolet region and the absorption maxima occurs at 257 nm.

The colloidal properties of the clay minerals have been used for hundred of years, especially in the manufacture of pottery and in foundry. A systematic attempt has, however, been made only in this century to understand the origin of their behaviour. Considerable success has been achieved in the past fifty years in regard to the search for high purity clays and for evidences of their crystallinity. The atomic structures of the common clay minerals have been to a great extent determined and applied to explain the properties of the individual members by numerous investigations. The structures of some of the clay minerals used in the present investigation are briefly discussed, indicating their differences from each other and their peculiarities, which are responsible for the special colloidal behaviour of the minerals. The vast majority of the natural soils contain in the clay minerals viz. kaolinite, montmorillonite, illite, chlorite, vermiculite and mixed layer-lattice type minerals.

On the basis of crystallo-chemical character of these clay minerals, the correlation between the structure and the exchange properties has been established from the important research contributions of Pauling (10), Bragg (11), Gruner (12), Brindley (13), Hoffmann (14), Marshall (15), Hendricks (16) and others (17-23). From these studies, clay minerals are recognised to consist essentially of two structural units. One is composed of two sheets 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 to balance the structure giving the brucite structure which has the formula $Mg_3(OH)_6$. The second unit is the tetrahedrally co-ordinated silica. A silicon atom being placed at the centre of a regular tetrahedron is equidistant from four oxygens or hydroxyls. The silica tetra hedra are joined together in the a, b directions, through oxygen, to form a hexagonal network which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$. The tips of all the tetrahedra are in the same direction.

Kaolinite:

The kaolinite is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet 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 other in the c direction. During stacking the oxygens of the tetrahedral layer are placed very close to the hydroxyls of the octahedral layer, so that the sheets are held tightly by hydrogen bonding as a result of which very little expansion in the c-direction is possible.

Montmorillonite:

According to the currently accepted concept, montmorillonite is composed of units, made up of two silica tetrahedral sheets, with a central alumina octahedral sheet. All the tips of the tetrahedrons are point 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 this group are also developed by stacking of these unit sheets one above the other in the c-direction. During stacking, the O layers of one unit are close to the O layers of the other unit, so that there is an excellent cleavage between the sheets. Polar molecules can enter 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.

Vermiculite:

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 exchangable ions in between the mica layers. It has also been suggested that these exchangable 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 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 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

$$[Si_8]^{IV} \quad [Mg_{6-x}\ \underset{\underset{Mx}{\downarrow}}{Li_x}]^{VI}\ O_{20}(OH)_4$$

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

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

In certain Laponite products, there are no fluorine atoms in the structure, these are being replaced by hydroxyl ions. The layers (platelets) are about 10 A° thick and are extended in two dimensions. If the cations present were only silicon and magnesium, a single layer would be a 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 absorbed 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 which means the total number of exchangeable cations that a clay can retain per 100 gm.

Thus ion exchange sorption of inorganic as well as organic ions is known to occur in clay minerals (24, 25).

Hence the origins of the charge of the clay lattice are believed to be due to isomorphic substitution, lattice imperfections, broken bonds at the edges of the particles and exposed structural hydroxyls. The negative charge on the clay minerals is compensated by adsorption of cations. The 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 (26), Bar and Tenderloo (27), Hendricks and Alexander (28), Schachtschabel (29), Mukherjee (30) and others. Most of these investigations were based upon exchange equilibria, selectivity etc. with simple inorganic ions (31, 32). Exchange reactions involving clay minerals with organic compounds have also been established by different scientists (33-36).

Amongst earlier workers, Renold (37) (1936) was perhaps the first to study systematically the exchange behaviour of Cu, Pb, Ni, Ag, Zn, Hg and Cd permutites and observed an increase in the exchangeability of these cations in the order shown. Zn was found by him to be as effective as Ba in its exchanging power. Jenny and Engabaly (38) (1943) 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 (39, 40) have studied in detail the interaction of montmorillonite clay and trace element cations. They observed the release of the metal ions in the order $Zn^{2+} > Mn^{2+} > Ni^{2+} = Co^{2+} > Cu^{2+}$ from the clay surface by H^+. Moreover, quantitative measurements revealed that the amount released was much less than that adsorbed, so that a part of the adsorbed cations was considered to be "fixed". Martin and Glaeser (41) 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. Chakravorty and Laitinen (42) 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 (43-45) 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 (46) 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^0, may be used to correlate the relative affinities of the ions for the mineral while for the alkali metal ions only, $1/a^0$ may be utilised for the purpose. Thielmann and McAtee, Jr. (47) 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 seeving separation. The cation exchange process between tris (ethylene diamine) Co(III) and Na^+ on montmorillonite was studied by Knudson, Jr. and McAtee, Jr. (48) 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 (49) 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 (50) extended Gieseking's (51) 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 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 case. 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 (52), Mortland (53) and Theng (54). A number of general conclusions has emerged from these studies by Hendricks (50), Jordan (55), Cowan and White (56), Diamond and Kinter (57), Weiss (58), Greenland (52), Theng et al (59), Walker (60), Vansant and Uytterhoeven (61), [illegible] et al (62) 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 ($>$ C8), 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 [$d_{001} \sim 12.6 - 13.5$ 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 (63), Theng et al (59) and others.

The bipyridylium halides, diquat and paraquat, are perhaps the best known and most widely studied members of the cationic pesticide family, because of their versatile use as broad spectrum, contact herbicides all over the globe. Numerous scientists have contributed to the literature on the adsorption and desorption behaviour of diquat and paraquat with clay minerals and resins and their important findings are summarised below:

Weber et al (64) studied the interaction of diquat and paraquat with montmorillonite and kaolinite and noted that the herbicides were taken up by the layer silicates upto their exchange capacities. The adsorption isotherms belong to the H- or high affinity class of Giles et al (65) suggesting very strong adsorption and were insensitive to variation of temperature. The inferred that diquat and paraquat were adsorbed by an ion-exchange process, replacing an equivalent amount of Na^+ initially present at the clay surface.

Hayes et al (66) investigated the interaction of diquat and paraquat with Na^+, K^+, Mg^{2+} and Ca^{2+} forms of kaolinite, illite, montmorillonite and vermiculite and concluded that the dominant factor in adsorption on the minerals was a non-specific interaction between bipyridylium cations and the charged clay lattice and supported the belief of Knight and Tomlinson (67) that the fundamental mechanism of adsorption of both the herbicides on the minerals was cation exchange. From microcalorimetric study, Hayes et al (68) also reported that the adsorption of the bipyridylium ions on Na-bentonite is exothermic while in Na-vermiculite, the adsorption process is endothermic.

However, although the cation exchange is undoubtedly the principal mechanism underlying the uptake of these bipyridylium ions by clays and soils, recent ultra violet and infrared spectroscopic measurements by Haque et al (69, 70) have inticated that charge-transfer between the organic cation and the anionic silicate framework may also be involved.

X-ray diffraction studies (64) of the clay paraquat complex suggest that the herbicide cation is intercalated by montmorillonite and the plane of the rings lies parallel to the silicate layers, thus affording close van der Waals contact between the molecule and the clay surface. No interlayer penetration occurs with kaolinite, adsorption taking place only on external basal and edge surfaces of the crystals. This difference in the location of adsorption sites partly accounts for the observation that montmorillonite retains adsorbed paraquat much more firmly than kaolinite.

The general behaviours of the uptake and retention of paraquat by clays described above have been confirmed by the work of Tomlinson and co-workers (67,71). These authors have introduced the term "strong adsorption capacity" (SAC) which is the capacity of the adsorbent to reduce the amount of herbicide in solution to a level which is chemically undetectable. The practical usefulness of it is shown by the finding that the SAC corresponds to the capacity for herbicidal inactivation to within at 50 per cent (67).

Weed and Weber (72) have investigated in detail the effect of adsorbent charge and the kind of exchangeable cation initially present in montmorillonite, vermiculite and K^+-depleted micas on the adsorption characteristics of diquat and paraquat. They noted that the maximum exchange by montmorillonite was close to the exchange capacity of the sample being little influenced by the nature of the saturating organic cations, while vermiculite adsorbed appreciably less than its exchange capacity and only 13 per cent of the exchange capacity of the muscovite sample was satisfied with the herbicide cations. Moreover, the extent of adsorption with vermiculite depended on the saturating inorganic cations decreasing in the sequence $Na^{+} > Ca^{2+} \geqslant Mg^{2+}$.

In order to examine more clearly the influence of surface charge density of the adsorbent on the competitive adsorption by ion exchange of diquat and paraquat when these organic cations are both present, Weed et al (73,74,75) determined the exchange isotherms for the herbicide cations on a series of 2:1 layer silicates with varying charge densities. They observed that paraquat was preferred to diquat by all montmorillonites but with vermiculites of higher charge density, this preference was apparently restricted to the external crystal surface and a reversal was observed for the interlayer surface where diquat was preferentially taken up. The charge centres of the cations are 3-4 A° apart in diquat while it is 7-8 A° in paraquat (73). The preference for one or the other of the cations by the layer silicates was related to the geometric "fit" between the charges on the cation and those on the clay in that the cation whose charge centres could most nearly approach the adsorption sites on the mineral surface would be preferred. These results indicate that the negative charge on the layer silicate lattices are discrete and relatively fixed as proposed earlier by Edwards et al (76) and are not smeared out as suggested by some workers (77). If the latter were the case, the differential selectivity by various layer silicates for these two organic cations would not have been obtained. Philen and co-workers (74,75) have further extended the above analysis to a greater number of clay minerals and soil clays of varying charge densities. These workers observed a simple linear relationship between the charge density and the extent of adsorption of the organic cations when exchange is restricted to external crystal surfaces, such as in collapsed vermiculite and micas.

The phytotoxic effect and availability to plants and microorganisms of diquat and paraquat adsorbed on different clay mineral types have been studied by Weber and co-workers (78, 79,80,81). These authors have noted that these organic cations in the adsorbed state with montmorillonite cannot significantly inhibit the growth of young plants such as cucumber seedlings (78,79) or be decomposed by microorganisms (80) while these herbicides when adsorbed on kaolinite and vermiculite can be slowly released to the surrounding medium and thus affect plant growth. This is due to the fact that these herbicide cations are intercalated by montmorillonite where as in kaolinite, adsorption is restricted to external surface only (82,71). With vermiculite, however, although interlayer penetration occurs, the extent of intercalation is limited as complete exchange for the inorganic ions initially present is not achieved. Diquat present at montmorillonite surfaces may, however, be made available to plants on addition to the system large organic cations like N-(4-pyridyl) pyridynium ions capable of displacing the adsorbed herbicide (71).

The desorption characteristics of the various samples of the herbicide complexes showed marked differences and apparently there has not been unanimity about the displacement of the herbicide from the adsorbed state. Funderburk et al (9, 83) showed that elution of adsorbed paraquat and diquat by a saturated solution of ammonium ions did not occur with montmorillonite or bentonite although it did with a soil sample and with kaolinite. Weber and Scott (73) found that the adsorbed herbicide could be displaced from kaolinite by 1 (N) Barium Chloride. However, Dixon and co-workers (84) reported that some displacement of diquat from montmorillonite was possible when molar solutions of K ions were used as the eluting agent. It seems likely that some of those differences in behaviour were due to differences in concentration of the cation and the extent to which the clays were saturated with the herbicide.

Malquori and Radaelli (85) compared the relative effectiveness of NH_4^+, K^+, Ca^{2+}, Mg^{2+} and Na for releasing paraquat previously adsorbed on five different clay minerals at varying concentrations. K^+ and NH_4^+ were, in general, more effective than the other cations studied, but no paraquat was released when its concentration on the clay was below a certain limit, which varied considerably with the type of the mineral. The release of diquat and paraquat from soils by ammonium ions has been used by Tucker, Pack and Ospenson (86) to define two degrees of adsorption to soil. At low concentrations, complete desorption of the herbicide is possible by boiling with 18 (N) H_2SO_4 ("tightly bound herbicide"). As the concentration increases, a portion of the diquat and paraquat can be desorbed by leaching with saturated ammonium chloride ("loosely bound"). At high levels, the unbound herbicide can be leached with water. The correlation of the binding strength of the herbicide with its availability to plants has been reported by Radaelli and Martelli (87). Corbin, Upchurch and Selman (88) showed that the phytotoxicity of diquat and paraquat in highly organic soils decreased when the pH was increased.

The adsorption and desorption behaviour of diquat and paraquat on eight arid-zone soils of Sudan were studied by Gamar and Mustafa (89). They observed that the sorption data of the herbicides conformed quite well with the linear form of Langmuir equation and less than 1 per cent and about 50 per cent of the adsorbed organic cations could be released with water and 1(M) $BaCl_2$ respectively. Moreover, the fact that the amount of herbicide retained against the successive extraction with 1(M) $BaCl_2$ solution nearly equals the SAC values of the soils used led the authors to suggest that the adsorption of these organic cations involves two mechanisms.

One of these is dominant for the SAC region while other is dominant beyond that region. Weber and Scott (78) reported that less than 15% of the adsorbed diquat^{2+} or paraquat^{2+} was released from its respective complex with montmorillonite by a single equilibrium with approximately five symmetry of 0.005 (M) chloride solutions of Al^{3+}; Ca^{2+}; Mg^{2+} or K^{+}. On the other hand, upto 70% was desorbed from the corresponding vermiculite complexes. The actual proportion displaced depends on the kind of electrolyte used, decreasing in the order $Ca^{2+} > Al^{3+} > Mg^{2+} > K^{+}$ for paraquat. Differences in charge density and hence in intercharge separation on interlayer surfaces, together with variations in stability of cation - water assemblages in the interlayer space, were invoked by Wood and Weber (82) to account for these observations. Dixon et al (84) have also reported similar differences between montmorillonite and vermiculite complexes with diquat in their response to treatment with 1(M) KCl solutions. More recently, Narine and Guy (90) have studied the interaction of diquat and paraquat with bentonite and noted that the adsorption of both the herbicide cations was very sensitive to ionic strength variation and the adsorption decreased by 36% as the ionic strength increased from 0 to 0.5 moles/litre.

Guy et al (91) have also reported that the percentages of paraquat released from the bentonite complex by 0.1 (M) solutions of Ca^{2+}, Mg^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+} and Li were found to be 9.4, 8.0, 9.4, 8.7, 14.8 and 4.1 respectively.

Best, Weber and Weed (92) studied the competitive adsorption of diquat and paraquat on strong and weak cation exchange resins, and observed that diquat was preferentially adsorbed over paraquat by IR - 120 resin (strong acid) while the reverse effect was noted with the IRC - 50 resin (weak acid). Preferential adsorption was attributed to the relationship between surface charge density of the adsorbents and the cation charge spacings as well as steric hindrance due to the bulky size of these cations. Furthermore, Weber, Ward and Weed (93) showed that equilibration with deionised water did not remove detectable amount of diquat or paraquat from IR - 120 resin complex but both the herbicides were completely desorbed from the resin with 1 (M) Sodium Chloride solution.

On a molecular scale, the phenomenon of firm adsorption is associated with the shape and charge distribution of the paraquat ion. The two pyridine rings of paraquat can rotate about the interring bond and readily assumes a coplanar structure —— a prerequisite of herbicidal activity. This flat configuration undoubtedly facilitates their interaction with the clay mineral surfaces. Paraquat is highly polarisable and its normal charge distribution is distorted in the vicinity of the negatively charged clay surfaces thus charge transfer complexes are formed (69), reinforcing the normal coulombic attraction forces. Paraquat is readily displaced quantitatively from cation exchange resins (93) as distinct from clay minerals which further suggests that other adsorption forces, in addition to coulombic forces, are involved in the paraquat clay system.

So, it appears from the review above that although the adsorption characteristics of the bipyridylium herbicides on different clay minerals and cation exchange resins have been extensively investigated from various angles, similar studies on Laponite (a synthetic hectorite), chlorite and molecular sieve are still lacking. The desorption characteristics of the herbicide cation from the adsorbent matrices have also not been very systematically studied with different inorganic and organic cations of varying size, shape and charge. Our knowledge of the physico chemical aspects of the desorption processes of the organic herbicide cation from the clay and resin 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 paraquat on and from bentonite, vermiculite, Laponite, chlorite, Amberlite IR - 120, Amberlite IRC - 50 and molecular sieve - 13X by monovalent and bivalent inorganic and organic ions of varying size and shape.

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 (94). A review of cation exchange equations as they are being used in soils and in other exchangers has been done by Bolt (95) and Helfferich (96) and their applicability to soils discussed by Babcock (97). 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 of the cation or anion exchanger has been assumed 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

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

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.

Weigner (98) 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, where as Weigner (98) showed that the position of equilibrium was independent of volume. Weigner and Jenny (99), however, in 1927, overcome the second objection and modifying the equation as

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

[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 (100), 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 (101)

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

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 $\left(\frac{x}{m}\right)_{max}$ is the monolayer capacity.

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

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

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 to the Langmuir's with two constants were proposed by Vageler (102, 103) 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 (102) 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 of 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 (98).

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 (104) and Gapon's (105) equations as a starting point (95). 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 (106).

The ion exchange formulations are usually based on three theories i.e. (i) crystal lattice theory (ii) double layer theory and (iii) Donan membrane theory (107). 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 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 hetrogeneous systems are analogous to the laws governing the solutions of electrolytes.

Jenny (108) envisaged a kinetic condition on the surface and derived from statistical approach the equation below.

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

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 (102, 103).

A more refined approach was introduced by Davis (109,110) and applied to exchange on soil clays by Krishnamoorty and Overstreet (111). 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, eg, 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 Ganssen (112) and Kerr (104), investigating specific mass action equations for uni- univalent and uni- bivalent exchanges as

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

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

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 empirically. Bauman (113) and Gregor (114) pointed out the difficulties in terms of swelling and volume change particularly of the resins. The model introduced by Gregor (114) although thermodynamically less well-established, brings out clearly the physical action of the swelling pressure. A more rigorous application of the law of mass action has been made by Boyd and co-workers (115) in which the "solid solution" idea of Vanselow (116) 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 (117) 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 Wiegner 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 (118, 119). 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 reactions involving interlattice sites.

Attempts to understand ion exchange reactions on the basis of electrical double layer, as postulated by Mukherjee (120) 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 (121), Mitra and Bagchi (122), Ganguli and Mukherjee (123) and Chakravarti (124).

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 (125,126). 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 (127) and further advanced by Shainberg and Kemper (128,129). Extension of this model to hetrovalent 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 (128,129) is of great interest as an effort 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 (130, 131,132) 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 (133), Kalchatsky (134) and others.

In the present thesis, an attempt has been made to fit the adsorption data of paraquat on bentonite, vermiculite, chlorite, Laponite, cation exchange resins and molecular sieve in the Langmuir equation and the desorption data of the herbicide cation (paraquat^{2+}) from its respective adsorbent complexes by monovalent and bivalent inorganic ions in the model of Pauley (135).

Pauley's Model:

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

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

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

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

$$\Delta G^{\circ}_{1} = \int_{a^{\circ}_{A}}^{\infty} \frac{e^{2}}{r^{2}\epsilon}\, dr = \frac{e^{2}}{a^{\circ}_{A}\epsilon} \qquad .. (3)$$

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

where ΔG_1^0 and ΔG_2^0 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^0 = distance of the closest approach between counter ion 'i' and fixed ionic group. Hence the overall free energy change for the whole process is

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

and the thermodynamic equilibrium constant K_A^B is

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

In the exchange of various univalent counter ions 'i' for an arbitrary univalent reference ion A, a linear relationship should exist between ln K_A^B and $\frac{1}{a_i^0}$.

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 counterionwith smaller a^{o} values and higher valency.

SECTION - C

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

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 (106). 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 (eg. 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 (136,50,96). 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 (96). 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 polarisability, (b) with decreasing ease of cation hydration and (c) with increasing counterion charge.

The above criteria, however, do not hold good in cases where some specific interactions take place. In accordance with the above observations, the order of increasing preference of alkali metal ions for ion exchange onto montmorillonite (39, 114, 137-156), vermiculite (157) and kaolinite (158, 159) is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The exchange of NH_4^+ is complicated by physical adsorption of ammonia (160) and fixation of NH_4^+ ion (161). It was observed that NH_4^+ is held more strongly than Na (162) or even Rb (163).

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 (164,165). It was reported that H^+ is apparently preferred over some divalent cations in ion exchange on montmorillonite and clay soils(143, 166) and over caesium on vermiculite (167). The reported relation orders of exchange on montmorillonite are $H^+ < Cs^+$ (143), $K^+ < H^+ < Ca^{2+}$ (137) and $K^+ < NH_4^+ < H^+ < Mg^{2+}$ (40). Under conditions which minimise dissolution of clay by acid attack, the corresponding orders were $H^+ < Na^+ < K^+$ (140) and $Na^+ < H^+ < NH_4^+$ (162). The sequence of exchange of alkaline earth ions on clays has generally been reported as $Mg^{2+} < Mn^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (140, 143, 162, 167 - 177). The reverse order is sometimes found in vermiculite (174, 178, 179). For the exchrage of divalent transition metal cations on clays, the reported orders of preference are $Mn^{2+} \simeq Ni^{2+} \simeq Fe^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$ (180), $Ca^{2+} < Co(II)^{2+}$ (181) and $Ni^{2+} < Ba^{2+}$ (176). 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 (40, 137, 141, 143, 146, 147, 166, 169, 173-175, 181-186) although there is exception to this trend. In the usual general purpose cation exchangers, the selectivity sequence of the most common cations is $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+} > Tl^+ > Ag^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+$ (187-190).

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 (50) may operate. Studies on the replacement of exchangeable sodium and calcium from montmorillonite by various alkyl ammonium cations were made by Theng et al (59). They found that the affinity of the clay for the organic cation 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 by the alkyl ammonium ions than was Ca^{2+}. In studies in which the alkyl ammonium ion is replaced by metal cations, Mortland and Barake (191) showed that the order of effectiveness in replacing ethylammonium ion was $Al^{3+} > Ca^{2+} > Li^+$. 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 interlameller position begins, it is completed before ethylammonium ions from other layers are exchanged. Similar observations have been reported by Barrer and Brummer (63), McBride and Mortland (192) and Theng et al (59). The exchange of various alkylammonium cations from aqueous solution by Na-Laponite has been carried out by Vansant and Peeters (193). 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 (52) and also to the change in hydration state of the ions in the clay interlayer (61, 62).

Charge density of the clay mineral may also affect the orientation of adsorbed organic cations through steric effects. Thus, Serratosa (194) 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 A^{o}. On the other hand, pyridinium-vermiculite has the pyridinium cations vertically positioned with respect to the clay platelets and a d_{001} spacing of 13.9 A^{o}. 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. 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 interlameller regions of swelling clay minerals.

The sequences of the univalent and bivalent cations overlap in resins of high capacity and moderate and high degree of cross-linking. For strong acid resins, H^+ usually falls between Na^+ and Li^+. For weak acid resins, the position of H^+ depends on the acid strength of the fixed anionic groups. The selective uptake of Li^+, Na^+ and K^+ by a series of methacrylic acid cation exchange resins of various divenyl benzene contents was measured by Gregor (195) et al. The general order of preference was $Li^+ > Na^+ > K^+$. This preference become more marked as the degree of neutralisation of any given resin increased. This resin behaviour was compared by the authors with the association evidenced by the alkali metal acetates.

Studies on the ion exchange equilibria in resins by various workers (196, 197) have revealed that the selectivity order of a cation exchanger polymer is influenced by many factors such as the structure of the polymer, the more fraction of the exchanging cations in the polymer phase and the changing field strength of the fixed exchange sites, i.e. by the charge and polarising power of the cation and the polarisability of the fixed anionic sites and that of the solvent medium (198). Thus, the affinity sequence of the alkali metal cations in their exchange reactions in aqueous solutions on crosslinked polymethacrylic acid exchangers has been shown to be the reverse of that with polystyrene sulphonates (199, 200) where the order is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. It has been suggested that in polymethacrylates, specific association between the counterions and the fixed ionic groups, i.e. site binding (201), takes place and is accompanied by the release of water molecules from the solvation shells of the participating species. With polystyrene sulphonate exchangers, however, it has been inferred that ion water interactions (200) are of prime importance in determining the order of alkali metal cation selectivity.

Lindenbaum and Boyd (201) obtained an increase in entropy in the exchanger of Li^+ for Cs^+ in crosslinked polymethacrylate exchangers and this preference for Li^+ has been explained by assuming a specific association, i.e. site binding between Li^+ and the carboxylate group of the exchanger with the release of water molecules. Further, dilatometric measurements by Strauss and Leung (202) with linear polymethacrylate have shown that a volume increase of approximately 5 ml per equivalent occurs in the system when tetramethyl ammonium counter ions are replaced by Li^+ or Na^+. If water is released in site binding, an appreciable positive contribution to ΔS^0 also could be expected (203). These effects have been ascribed to a competition between water of hydration and anion for a position near a given cation and ultimately to the charge distributions, polarisabilities and the effective field strengths of the participating ions (204).

Sarkar and Das Kanungo (205) have recently studied the desorption characteristics of tris- trimethylene diamine Co(III) i.e. $Co(tn)_3^{3+}$ from its Amberlite IRC -50 resin complex by monovalent inorganic ions and noted that the exchange isotherms are of the S-type (206) indicative of cooperative sorption and the exchanging efficiency of the ions in aqueous medium is in the order : $NH_4^+ > Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. They also observed that the plots of log (selectivity coefficient) against both the hydrated ionic radius and the reciprocal of the Debye Huckel ion- size parameter, a^0, of the monovalent ions are linear suggesting that both the parameters may be used to correlate and predict the relative affinities of the alkali metal cations for the resin matrix.

The structure and ion-exchange properties of the synthetic zeolite molecular sieves has been well reviewed by Breck (207) and Barrer (208). The exchange equilibria and selectivities of alkali and alkaline earth and rare earth ions for different zeolite ion-exchangers have been described by Barrer (209), Sherry (210) and Maes and Cremers (211). Their results have led to the conclusion that there is more extensive ion binding in X-zeolite as compared with Y-type, which has a higher silica content and a lower total exchange capacity. The effect of different silica to alumina ratios on cation selectivity has also been observed by Ames (212, 213) for a number of naturally occurring and synthetic zeolites. The crystal structure of zeolite -X and Y enclose three different kinds of interconnecting cavities in which the exchangeable cations are located on different crystallographic sites (214-216). Sherry (210) has interpreted his exchange isotherms in terms of the distribution of Na ions over different crystallographic sites as revealed by the early X-ray studies of Broussard and Shoemaker (214) and summarized by Breck (216). Since the cavities are entered by windows of definite dimensions, steric and ion sieve effects have been observed in exchangers involving large cations (210, 209). The intracrystalline space may be filled by these large cations before complete replacement of the ions initially present, is achieved. Hence, the extent of exchange may also be limited by the space requirement of the cations (209).

Barrer et al (209), Theng (217) and Vansant et al (218) studied the exchange adsorption of ammonium and some of its alkyl derivatives in different natural and synthetic zeolites. They observed that for steric reasons, none of the alkyl ammonium ions could effect a complete replacement of Na initially present in the zeolite, so that the exchange reaction was confined to the large cavities in the crystal. The maximum extent of exchange decreased with an increase in molecular weight and polarizability of the cations but was always below the limit imposed by the space requirement of the respective ions. This decrease was also greater for the di and tri alkyl derivatives than for monoalkylammonium ions of comparable molecular weight, and was more pronounced in X than in Y zeolites. The importance of the affinity of cations in determining the upper limit to exchange was further shown by the observation that for a given alkyl ammonium ion, this limit decreased with an increase in the affinity of the inorganic ion which it replaced from the zeolite, the order being $Li^+ > Na^+ > K^+ > Ag^+ > Tl^+$. Vansant and Vanhoof (219) recently studied the exchange of alkanediammonium ions in the zeolites X and Y. They concluded that for steric reasons, none of the organic cations could effect a complete replacement of Na^+ ions initially present in the zeolites. For any given alkane di-ammonium ion, the maximum exchange capacity decreases with an increase in the affinity of cations initially present in the zeolite, the order being $Li^+ > Na^+ > K^+$.

The ion exchange behaviour of some transition metal ions in synthetic zeolite X was studied by Maes et al (220) and they found that the overall selectivity of both X and Y zeolite for bivalent transition metal ions increases in the order $Ni^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$. In addition to the hydration characteristics and ionic radius, the exchange is governed by the coordination ability of the transition metal ion. Hence the more important characteristic of exchange studies are:

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

(ii) Obedience to the Langmuir equation of the data on exchange sorption of large organic molecules. A simple equivalent fraction exchange equation has been proposed to fit in the exchange data of Na^+, K^+, Ca^{2+} on bentonite (221) 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 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 (222). 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 Chakraborty (223-226) 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, the desorption of the organic paraquat ion has been studied with tetra-alkylammonium, alkane diammonium and long-chain surface active ions of varying size and shape.