GENERAL INTRODUCTION
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Soil which is the most important material covering the outermost layer of the earth's crust is a heterogeneous polydisperse system of solid, liquid and gaseous components of various properties. It possesses distinct morphological, mineralogical, chemical and physical properties resulting from certain inheritance factors, from its unique position on the surface of earth and from the environmental factors existing at that position.

Soil is very complex in nature and consists of four important constituents viz. air, water, organic and mineral matter. The mineral matter consists of particles generally less than 0.002 mm and is called the clay fraction of the soil while the coarse fraction consists of rock debris and sand. Being the most reactive portion of the soil, clays are involved in many physico-chemical reactions. Due to their colloidal properties the clay fraction of the soil has since long claimed the interest of soil scientists, mineralogists, geologists, chemists and others.

X-ray and other studies have revealed that clay is crystalline in nature and composed of simple building units. The difference in the properties of clay is believed to depend on the spatial arrangement of these units in the crystal lattice. Treatment of the general subject of clay mineralogy has been given by Marshall¹, Grim², Van Olphen³ and Gieseking⁴. The clays are composed of alternating, parallel, two dimensional layers formed from silicate tetrahedra and
aluminate octahedra. The deposition of these layers and the extent and nature of isomorphous substitution determine to a great extent the chemical and physical properties of the mineral. The silicate clays contain at least six different groups of minerals viz. kaolinitic, montmorillonitic, illitic, vermiculitic, chloritic and attapulgitic. Some important clay minerals are described below.

**KAOLINITE**

The mineral is composed of a single tetrahedral sheet of silica and a single octahedral sheet of alumina combined in a unit so that the tips of silica tetrahedral and a layer of octahedral sheet form a common layer. The mineral thus has a 1:1 non-expanding lattice, where two adjacent units are held together rigidly by hydrogen bonds. Cations and water cannot enter these lattices. These clays have therefore low swelling properties. Plasticity, cohesion and shrinkage properties are also very low.

Its structural formula is \((\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{10}\). The size of the unit cell is 7.2 Å. The general shape of the mineral is that of a thin plate hexagon. It possesses a low exchange capacity of about 5-10 meq. per 100 g. Halloysite, nacrite, dickite and anauxite are some other isomers of the kaolin group.

**MONTMORILLONITE**

The mineral was first studied by Le'chatelier\(^5\) and has been assigned the formula \((\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot 12\text{H}_2\text{O}\). Ross and his colleagues\(^6\) established the identity of montmorillonite as a definite clay mineral
I(a) Diagrammatic edge view of kaolinite showing two complete layers. The respective crystal units are bound to each other tightly by an oxygen-hydroxyl linkage, thereby giving a restricted and non-expanding lattice. The adsorptive capacity is limited.

I(b) Diagrammatic edge view of montmorillonite showing two complete layers. The respective crystal units are loosely bound to each other by weak oxygen linkages which allow wide expansion of the lattice. There is high internal adsorption of water and cations.

I(c) Illite has the same general structural organization as montmorillonite except in respect to the linkages between the crystal units. Here K atoms supply additional connecting linkages between the crystal units, thus supplementing the oxygen bonding. The expansion is sharply lessened by K linkages and adsorptive capacity of the clay lowered.

Crystal unit 9.3 A
Distance variable
Internal adsorptive surfaces

Crystal unit

Fig. 1
species. Structurally the mineral consists of three layers, a central octahedral alumina sheet enclosed between two silica tetrahedral sheets, imparting a 2:1 layer lattice structure. The alumina and silica sheets are held together by common oxygen atoms. The layers are stacked one above the other in the C direction. There is a very weak oxygen-oxygen bond and an excellent cleavage between the units. On account of this weak bond, the outstanding feature of montmorillonite structure is that water and other polar molecules can enter between the unit layers causing the lattice to expand in the C direction. The lattice structure of these minerals, unlike that of kaolinite is not fixed and the c-axis dimension of montmorillonite varies from about 9.6 Å, when no polar molecules are in between the unit layers, to substantially complete separation of the individual layers in some cases. This 2:1 layer structure of the clay is also responsible for high plasticity, cohesion, swelling and marked shrinkage, besides the high cationic adsorption capacity which varies from 70 to 100 meq. per 100 g clay.

There are substitutions, within the lattice, of aluminium and possibly phosphorus for silicon in tetrahedral coordination and of Mg, Fe, Zn, Ni, Li etc. for aluminium in the octahedral sheet. Total replacement of aluminium by magnesium, iron and chromium yields the minerals saponite, nontronite, volkonskoite and sauconite.

ILLITE

The basic structure unit of illite is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The
2(a) Kaolinite, a 1:1 layer silicate mineral

2(b) Montmorillonite, a freely expansible 2:1 layer mineral. The inter-layer cations are freely exchangeable.

2(c) Illite structure is similar to 2(b) except that the electrical imbalance is set right by the presence of K ions situated between adjacent layers so that the net charge is 0.
unit is the same as that for montmorillonite except that some of
the silicons are replaced by aluminium and the resultant charge
deficiency is balanced by potassium ions. The unit layers extend
indefinitely in the a and b directions and are stacked in the c
direction. The potassium ions occur between unit layers where they
just fit into perforations in the surface 0 layers and exert a
definite stabilizing effect on the crystal lattice. Hence illite
crystals are less expandable and properties like hydration, cation
adsorption, swelling, shrinkage, plasticity and ease of dispersion
are less intensively developed than in montmorillonite.

The structural formula of the mineral is
\[(OH)_{4}K\{(Al_{4}Fe_{2}Mg_{8}Mg_{6})_{0}(Si_{8}Al_{4})_{0.20}\}\]. Basal spacings are of the
order of 10 Å.

The cation exchange capacity of this mineral varies from
0 meq. to 40 meq. per 100 g clay.

SOIL ORGANIC MATTER

The biosphere is an important and active soil forming agent.
It includes diverse elements like vegetation, microorganisms and
animals. The activities of these agencies give rise to accumulation
of organic matter in soil. Soil organic matter is very complex in
nature. The brown colored, high molecular weight components of
soil organic matter are commonly called humic and fulvic acids. The
organic matter shares the colloidal property of the soil and plays
a very important part in determining the qualities of a soil. Acting
as a binding agent it helps to improve soil structure, water holding capacity and tilth. Organic matter also tends to control and limit development of harmful alkaline conditions by neutralising the effect of some of the alkaline salts. Soils containing less than one percent of organic matter are generally considered to be poor in fertility and may need to be supplied with extra application of organic manures to bring up the organic matter content to a satisfactory level.

Humus material which occurs in soil as the result of microbial decomposition of organic matter, possesses several types of functional groups which are capable of attracting and dissociating hydrogen ions. The strength of the acid produced will depend upon the nature of the predominant groups present. Humus may also react with iron and aluminium ions to form complexes which may subsequently undergo hydrolysis to yield hydrogen ions. During the breakdown and mineralization of material like water, carbon dioxide, various salts and organic acids may be produced thus affecting or adding to the total acidity of the system.

**PHYSICO-CHEMICAL PROPERTIES OF CLAYS**

Clay fraction of the soil containing particles less than 0.002 mm in size, possess properties very much like those of typical colloidal substances. Hence these particles are known as soil colloids. They are responsible for the physico-chemical properties of soil.

The crystal unit of the clay particle forms a very complex
anion exposing a highly negative surface and is known as micelle. It attracts the positively charged cations and results in the formation of an electrical double layer where the negatively charged micelle constitutes the inner ionic layer and the loosely held cations surrounding the negative nucleus, form the outer layer. When such particles are dispersed in water the cations get hydrated and then dissociate to a certain distance from the surface, finally leading to the formation of a diffused electrical layer. In other words, a suspended clay particle may be compared to a dissociated electrolyte, the size of its ion falling within colloidal range.

Colloidal clay develops negative charge in two ways. Broken bonds around the edges of the silica-alumina units give rise to unsatisfied charges. The dissociation of hydrogen from hydroxyl groups attached to silicon in silica sheets leaves residual oxygen carrying a negative charge. Another way in which the negative charge is developed is due to the isomorphous substitution of trivalent aluminium for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium for trivalent aluminium in the octahedral sheet within the lattice structure.

Clay suspension can neither be classified as purely lyophilic nor as purely lyophobic colloids. They can be placed intermediate between the two well defined classes. In view of the importance of physico-chemical properties such as electrometric behaviour at reversible electrodes, ionic adsorption and exchange, thermodynamic equilibrium, zeta potential, viscosity and clay organic interactions,
their critical study can provide results of great significance in the investigations of clay minerals.

**SOIL pH**

Soil reaction (pH) is an indication of the acidity or alkalinity of the soil and is measured in pH units which vary from 0 to 14 with pH 7 as the neutral point. Mathematically, 

$$\text{pH} = - \log [H^+]$$

Acidity in soils arises from several different sources like presence of humus, nature of the alumino silicates in clays and their hydrolysis, presence of hydrous oxides and other soluble salts. Strongly acid soils (pH 4.0 to 5) usually have high and toxic concentrations of soluble aluminium and manganese.

Soils unleached or high in calcium (low rain fall areas) have pH values up to 8.5. With increased exchangeable sodium, soils may reach values over pH 10. Plants on soils with pH greater than about 9 usually have reduced growth and sometimes even die. The soil pH affects the activity of microorganism which also ultimately influences the plant growth.

**ION-EXCHANGE**

Ion exchange is a reversible process by which cations and anions are exchanged between solid and liquid phases if they are in close contact with each other. The clay minerals have the property of sorbing certain cations and anions and retaining these in an
exchangeable state and in most of the reactions they behave as ion-exchangers. The exchange reaction is stoichiometric. The exchangeable ions are held around the outside of the silica-alumina clay mineral structural unit and the exchange reaction generally does not affect the structure of the silica-alumina packet.

The property of ion exchange and the exchange reaction are of great fundamental and experimental importance in all the fields in which clay materials are studied and used. Chemical and physical processes in clays and soils are more or less intimately connected with ion exchange and this includes weathering of minerals, nutrient absorption by plants, swelling and shrinkage of clay and leaching of electrolytes. Ion exchange may therefore be considered as the most important of all the processes occurring in a soil.

Soil particles having the power to bind both cations and anions are amphoteric in character. The presence of anions can be demonstrated by electrophoresis. The negative charges created by isomorphous ion substitution are more uniformly distributed in the plates or lath shaped clay particles whereas the charges created by ionisation of hydroxyl groups attached to silicon of broken tetrahedron planes, are at corners and along edges. In addition to these two, negative charges may also originate from humic, phosphoric and silicic acids constituting more or less an integral part of the clay particle surface.

The amphoteric nature of the clay fraction requires the
existence of positive charges which may originate from hydrous oxides of iron, aluminium and manganese and from exposed octahedral groups which react as bases by accepting protons from the surrounding soil solution, thus acquiring a positive electric charge. The basic groups of humus are due to nitrogen.

The capacity of soils to adsorb and exchange cations and anions varies greatly with the content of clay and organic matter and the mineralogical composition. The cation exchange capacity is defined as the amount of a cation species bound at pH 7 or another suitable pH depending on the method used for its measurement. It varies slightly with the bonding strength of the ion and increases with the content of clay and organic matter. There are a number of factors which control cation exchange in clay minerals and therefore no high degree of accuracy can be claimed in the determination of cation exchange capacity.

Since the cation exchange is a stoichiometric reaction it follows the laws of mass action and therefore increased concentration of the replacing cation causes greater exchange by that cation. Kelley and Cummins\(^9\) found that the replaceability of Ca\(^{+2}\) and Mg\(^{+2}\) by Na\(^{+}\) increased as the concentration of Na\(^{+}\) in the solution increased. The complexity of this factor is shown by the data brought out by Kelly\(^10\). Other things being equal the higher the valence of the ion, the greater is its replacing power and the more difficult it is to displace when already present on the clay. Hydrogen is an exception. For the most part it behaves as a divalent or a trivalent ion.
Wiegner and Jenny\textsuperscript{11} suggested that the size of the non-hydrated ion controls replaceability. Wiegner and Jenny\textsuperscript{11} and later Atlen and Kurmies\textsuperscript{12} have presented strong evidence that all the common cations are hydrated and that hydration is important in exchange reactions.

It has been indicated by Hofmann and J.Endell\textsuperscript{13} that heating to moderate temperatures not only reduces the cation exchange capacity but changes the relative replaceability of the cations. It has been demonstrated by a number of workers that there is not a single replaceability series characteristic of all clay materials but separate replaceability series for the various clay minerals. The replaceability of NH$_4^+$ from kaolinite, montmorillonite and muscovite by various cations at various concentrations was studied by Schachtschabel\textsuperscript{14}. These data show that for NH$_4^+$-montmorillonite, H$^+$ and K$^+$ are about equally exchangeable, that all the univalent cations except Rb$^+$ and Cs$^+$ are more exchangeable than the divalent ions and that all the divalent ions have about the same replaceability. For NH$_4^+$-kaolinite, the exchangeability of cations is about the same as for NH$_4^+$-montmorillonite.

Barshad\textsuperscript{15} has investigated the cation exchange characteristics of vermiculite and has shown that the exchange process is reversible between Na$^+$, Ca$^{+2}$, Mg$^{+2}$ and K$^+$ but is not completely reversible between K$^+$, NH$_4^+$, Rb$^+$ and Cs$^+$. The latter tend to become fixed and are relatively non-replaceable.
ION-EXCHANGE ISOTHERMS

Ion exchange equilibrium can be characterized by the ion exchange isotherms. These isotherms are a graphical representation which, in principle, cover all possible experimental conditions at a given temperature. Equilibrium can also be described in terms of a quantity such as the separation factor, selectivity coefficient or distribution coefficient. As a rule, these quantities vary with experimental conditions. Ion exchange isotherms shows the ionic composition of the ion exchanger as a function of the experimental conditions. Various ways of representation can be used. To describe ion exchange processes and predict ion distribution several formulae have been proposed in the course of ion exchange studies.

Exchange situation as a distribution function (similar to partition of molecules between two solvents) was utilised by Rothmund and Kornfeld. The expression given by them

\[
\frac{[\text{Cation I}]}{[\text{Cation II}]}_{\text{Substrate}} = K \left( \frac{[\text{Cation I}]}{[\text{Cation II}]} \right)_{\text{Solution}}^n
\]

is a two constant equation.

According to the present opinion the structure of the diffuse double layer and its relationship to the surroundings is dependent on the active mass (the activity) of the diffusible ions and also connected with the changes in free energy. Therefore law of mass action can successfully be applied to the study of ion exchange.
Specific monovalent-monovalent and monovalent-divalent exchanges were investigated by Kerr\textsuperscript{17} with the expression,

\[
\frac{(Na-Soil) (K^+)}{(K-Soil) (Na^+)} = K_1 \quad \frac{(K-Soil)^2 (Ca^{+2})}{(Ca-Soil) (K^+)^2} = K_2
\]

Values of $K_1$ were usually constant over a narrow to moderate range whereas $K_2$ was found to be less satisfactory. $K_1$ often denoted as $K_s$, is also termed as selectivity constant or selectivity number and it is now recognised as a function of the ionic composition of the solid phase.

The equilibrium constant for mono-divalent exchanges was found unsatisfactory by Kerr. Vanselow\textsuperscript{18} showed that effective concentration within the substrate phase be taken as proportional to its mole fraction. In the mono-monovalent case, the dividends cancel and the Kerr equation remains. In the mono-divalent exchange (as for NH\textsubscript{4}-Ca case) the equation becomes,

\[
\frac{(NH_4^+)^2 (Ca-Soil)(Ca-Soil + NH_4-Soil)}{(Ca^{2+})(NH_4-Soil)^2} = K
\]

Applying kinetics to the equation for mono-divalent cation exchange e.g. for NH\textsubscript{4}-Ca exchange, Gapon\textsuperscript{19} showed that

\[
\frac{(Ca^{2+})(NH_4-Soil)}{(NH_4^+)(Ca-Soil)} = K
\]
Further investigations showed that the equation derived by Vanselow and by Krishnamoorthy and Overstreet have yielded satisfactory equilibrium constants for exchange of metal cations on selected bentonite clay soil colloids and synthetic resins.

**ADSORPTION**

The term adsorption is applied to the condensation of molecules on the surface of solids. In the first adsorption type, the surface condensation is due to the more or less non-specific physical capillary phenomena, and the adsorption parallels the physical character of the adsorbent. This physical adsorption is a low temperature adsorption and is reversible. The second type, which appears to be due to primary valence forces, is relatively strong and specific, being largely independent of the physical character of the adsorbent and is essentially of a chemical nature. This chemical or activated adsorption is non-reversible and is known as high temperature adsorption.

The phenomenon of adsorption in colloids or clays is mostly confined to the surface of colloidal particles. In most cases adsorption takes place by exchange of ions. In fact, ion-exchange itself may be considered partly an adsorption and partly a desorption reaction for which the negative charge on clay micelle and the electric double layer formed around it are responsible.

The adsorption of ions is governed by the type and the nature of the ion, the ion concentration and the type of the colloidal
particle. In the case of cations, the higher the valence of the ion, the more strongly it is adsorbed and more difficult in its replacement or exchange from the colloid particle. For cations of the same valency, the higher the atomic weight the greater is the adsorption. Hydrogen ions, however, behave as polyvalent ions. They are adsorbed more strongly than even divalent ions.

The property of adsorption plays an important role in soil fertility. It is due to this property that a soil is able to hold water and plant nutrients and keep them available for the use of growing plants and thus enables the soil colloid to function as a reservoir of nutrients for plant use. The study of the adsorption is important in understanding the mechanism of interaction of simple organic molecules and pesticides used in soils and clays.

Chemically soils are alumino silicate systems and as such are characterised by possessing exposed surface rich in oxygen atoms and hydroxyl groups. These surfaces are highly polar in character and possess an intense residual force. Generally these forces are responsible for holding the other ions or molecules at the surface temporarily or permanently depending on the forces operating at it. Residual valence forces, dipolar attractions or any other physical forces of the van der Waals type lead to adsorption, where the molecules are held temporarily, while chemical or electrostatic forces give rise to a permanent binding and molecules stay permanently on the surface.

In recent years numerous papers have been published on
organo clay complexes\(^{21-23}\). For those organic compounds possessing a basic chemical character and containing a \(\text{N-H}\) group, adsorption could occur by formation of a hydrogen bond between the amino group and the oxygen of clay surface. This would be a prime mechanism for the adsorption of the molecular form of the basic organic compounds. The adsorption of dimethyl amine\(^{24}\) and aliphatic amines\(^{22,24,25}\) by montmorillonite has been postulated to occur by such a mechanism.

With regard to the adsorption of aniline, the work of Swoboda and Kunze\(^{26}\) and Harter and Ahlrich\(^{27}\) indicates that aniline can be adsorbed by protonation at or near the surface and by base saturated clays due to dissociation of the proton in residual water on the clay surface and subsequent protonation.

Studies in the relationship of adsorption and desorption of pesticides from soils and clays are useful, in order to improve our understanding in this regard as well as in the role of fixation and release in plant nutrition.

**ADSORPTION ISOTHERMS**

The fundamental investigations on adsorption specially at the liquid-solid interface proceeded very slowly. The Freundlich equation was applied to all types of isotherms limited to adsorption from dilute solutions\(^{28}\) and that could be described as

\[
x/m = KC^{1/n}
\]

where \(x/m\) = amount adsorbed, \(C\) = concentration of solution at
equilibrium, $1/n = \text{sorption intensity}$ and $K = \text{Freundlich constant}.$

The Freundlich equation is essentially empirical and based on no theoretical model. Kipling$^{29}$ presented a justification for its application to adsorption from dilute solutions. Besides the application of this equation to a number of chemical reactions, recently Bigger and Cheung$^{30}$ used Freundlich equation to the adsorption of phosphate by soils and also by Van Bladel and Moreale$^{31,32}$ to the adsorption of pesticides on soils.

A model for the chemisorption process was presented by Langmuir$^{33}$ in 1916 which was based on the assumption that in case of chemisorption the adsorbed layer is unimolecular in thickness and there existed a dynamic equilibrium between the adsorbed and unadsorbed gas molecules. Langmuir gave the equation,

$$\frac{C}{x/m} = \frac{C}{b} + \frac{1}{Kb}$$

where $x/m$ is the amount adsorbed per unit mass of the adsorbent, $C$ is the equilibrium concentration of solute in the solution phase; $b$ is the adsorption maxima or capacity parameter and $K$ is the affinity parameter showing the bonding energy of the adsorbate to that of the adsorbent$^{34}.$ The Langmuir equation was successfully applied to a number of adsorption processes. Recently its use for the P adsorption by soils$^{35-38}$ and for the adsorption of nemagon on montmorillonites$^{39}$ was reported. More recently it was reported by several workers$^{40-42}$ that in some cases more than one Langmuir
isotherm was required to describe the overall sorption data. The deviation in the isotherm arose due to the involvement of more than one reaction mechanisms on different sorption sites$^{41,43,44}$ in the overall adsorption. In such cases constants $K$ and $b$ for different parts of isotherms were calculated separately by regression analysis$^{43}$. Ryden et al.$^{45}$ developed a method for resolving compound isotherms into their distinct parts. Most recently Griffin and Au$^{46}$ developed a competitive Langmuir equation for lead adsorption on montmorillonite and the Langmuir isotherm obtained successfully resolved the data for four different weights of clay into a single linear adsorption plot.

From the thermodynamic considerations Gibbs derived an important relationship between the adsorption in the surface layer binding the two phases and the rate of change of the surface with change in concentration of the solute. This concept is now no longer tenable. An equation for a composite isotherm is proposed as follows:

$$\frac{n_0 \Delta x}{m} = n_1 (1-x) - n_2 x$$

This equation is found applicable to adsorption from all types of solutions of various concentrations and can also be accounted for multilayer adsorption$^{47}$. Thus in a few cases it was found that although the composite isotherm had a linear section yet the adsorption was two molecules thick$^{48}$. During chemisorption process it was normally supposed that preferential physical adsorption of
one component occurs on the top of the first layer. To account for
such cases the above equation was modified

\[
\frac{n_0 \Delta x}{m} = \left[ (n_1^{s})_{\text{chem}} + (n_1^{s})_{\text{phys}} \right] (1-x) - n_2^{s} x
\]

In general composite isotherms showed a smooth variation with
composition of solution. In some cases, however, steps and sharp
discontinuities were observed. These were attributed to the
appearance of a second layer of adsorbate on the top of the first or
due to a phase change in the adsorbate. Sharp breaks in the isotherms
could be due to the change in the orientation of the adsorbate.
Venturello had published a series of papers\textsuperscript{49-51} in which the
presented various adsorption isotherms of organic dyes and iodine
solutions by solid inorganic compounds like alumina, silica gel,
magnesium hydroxide and calcium carbonate. It was suggested that
different parts of the isotherm correspond to the adsorption of
molecules or ions with different bonding energies and also due to
heterogeneity in the distribution charges on the surfaces of the
adsorbent.

A classification of the different isotherms obtained during
adsorption was proposed by Giles\textsuperscript{52, 53}. The Langmuir L type curve
was obtained when there was no strong competition from the solvent
for adsorption sites on the surface and the solid had a high affinity
for solute. This type of isotherm was reported by Weber\textsuperscript{54} and
Bailey et al.\textsuperscript{55} in triazines. An 'S' shaped curve was obtained if
the solvent was strongly adsorbed, there being a strong intermolecular
attraction within the adsorbed layer and if the adsorbate was monofunctional. An 'H' shape occurred when there was high affinity between the adsorbate and adsorbent as in the case of very dilute solution during chemisorption or adsorption of polymers or ionic micelles. Generally a vertical initial part of H type isotherm along with a plateau was indicative of chemisorption as in the case of fatty acids\(^5\) and some nematocides\(^7\). A 'C' type curve was obtained when there was constant partition of the adsorbate between the solution and the adsorbent as in textile fibres. It was indicative of the availability of new sites as the solute molecules were adsorbed from the solution. Such type of adsorption isotherms were reported in many cases including for amino acids and some pesticides by Greenland\(^5\) and Singhal et al.\(^5\)

A number of isotherms showed steps as has been discussed above. In general the steps appeared to mark a phase change in the adsorbed layer on the onset of the formation of a second molecular layer after completion of the first.

A less common shape involved was a wave type. The change in slope occurred at a small value of adsorption indicated a form of cooperative adsorption and that was due to some degree of deformation in packing in the crystalline state\(^5\).

**THERMODYNAMICS AND CHEMICAL EQUILIBRIA**

Thermodynamics is the study of energy-transformations. All chemical as well as physical processes are invariably accompanied by energy changes and a study of chemical thermodynamics gives a
quantitative account of the energy effects on chemical processes. This information can be used in the prediction of chemical behaviour.

The subject matter of thermodynamics is based essentially on two fundamental laws regarding the interconversion of different forms of energy. Equations have been developed giving the variation with temperature and pressure of certain physical properties of substances. The derivation of exact conditions for spontaneous chemical reaction and chemical equilibrium is of more interest to a chemist.

Thermodynamic treatment has been extensively used for the study of the exchange phenomenon of ions in clays by several workers and also more recently by Singhal et al. Thermodynamic treatments have also been used for calculating thermodynamic parameters in the processes which are reversible and stoichiometric. However, the approach is not applicable to processes which are not fully reversible and stoichiometric. To study such processes Jurinak et al. have proposed an equation by which an adsorption process can be thermodynamically defined.

Bigger and Cheung have proposed a new method to evaluate the thermodynamic equilibrium constant (K). According to them

\[ K = \frac{\Lambda_s}{\Lambda_c} = \gamma_s \frac{c_s}{\gamma_c} \frac{C_s}{C_c} \]

where \( \gamma_s \) is activity coefficient of adsorbed solute, \( C_s \) is the
concentration in ug of the solute adsorbed per ml of solvent in contact with the adsorbent surface, $\gamma_s$ is the activity coefficient of solute and $C_e$ is the concentration in ug of solute per ml of the solvent in the equilibrium solution.

In thermodynamic studies, quantities like free energy, enthalpy and entropy help to understand the exact nature of a chemical process.

**Free Energy**

It is denoted by G or F and is the chemical analogue of potential energy of mechanical systems.

The change in the free energy ($\Delta G$) can be defined as

$$G_{\text{product}} - G_{\text{reactant}} = \Delta G$$

when $G = H - TS$, where $H$ is enthalpy, $S$ is entropy and $T$ is absolute temperature.

At constant temperature and pressure when $\Delta G = 0$, there is no preferential direction for the reaction i.e. it is at equilibrium. When $\Delta G$ is less than zero, (negative value) then spontaneous changes will occur in the system and reaction will be in forward direction. When $\Delta G$ is greater than zero, (positive value) the reaction in reverse direction will be spontaneous. If conditions are altered the reaction can proceed in the forward direction. Spontaneous changes can continue to occur in the systems as long as the free energy of the system can decrease i.e. until the free energy of the system reaches a minimum value. Thus a knowledge of free
energy changes is of great importance in the study of chemical reactions. The value of $\Delta G$ for adsorption processes\textsuperscript{73} is negative and of the magnitude of $\pm 1.0$ to $-4.0$ kcal/mole while for ion exchange processes it is of still lower magnitude.

**Enthalpy**

It provides the information about heat changes of a system. The heat of reaction of a chemical change is the difference between the enthalpies of the product and the reactants of a reaction when the number of molecules of the reactants indicated by the chemical equation have completely reacted, i.e.

$$\Delta H = H(\text{product}) - H(\text{reactant})$$

Among the different methods $\Delta H$ can be calculated by using van't Hoff isochore. It can also be calculated by plotting $\ln K$ vs $1/T$. In a chemical reaction, when $\Delta H$ is negative heat is lost by the reacting system and gained by the surroundings. It is then called the exothermic reaction. When $\Delta H$ is positive heat is adsorbed by the system and lost by the surrounding and the reaction is endothermic. $\Delta H$ also shows the relative strengths of bonds holding the particles of the reactants and the products.

**Entropy**

The degree of disorder of a system or its randomness is measured by a quantity called the entropy. The change in entropy ($\Delta S$)
can be defined by the equation,
\[ \Delta G = \Delta H - T \Delta S \]

where \( \Delta G \) is free energy change, \( \Delta H \) is change in heat content or enthalpy and \( T \) is absolute temperature. If the \( \Delta S \) value is positive the system has more disorder, the process is spontaneous and has a tendency to attain equilibrium. The more a system approaches equilibrium the greater is the disorder and irreversibility. When \( \Delta S \) value is negative it indicates that the system has become more ordered and there is loss in the degree of freedom.

Knowledge of the entropy changes provides information concerning structural changes, accompanying a given process and determines whether a reaction will occur or not.

REVERSIBILITY AND HYSTERESIS IN ION EXCHANGE REACTIONS

In ion exchange processes generally diffusion of cations between inner micellar solution and outer solution took place in equivalent amounts and therefore ion exchange processes were taken for granted as perfectly reversible. In fact, thermodynamic formulations of the ion exchange process were based on this assumption.

But sometimes in ion exchange, it was found difficult to reach a true equilibrium state. For the oppositely directed exchange

(1) \( R-A+B = R-B+A \)
(2) \( R-B+A = R-A+B \)

the equilibrium state was characterised by the quotients \( K_{AB}^{i} \) and
K\textsubscript{AB}, which however could attain the same value within a reasonable time. This phenomenon was called hysteresis.

In fact all processes which involved diffusion into microporous solids were apt to show hysteresis effects which were attributed to slow approach to the final condition of equilibrium. But in clay and soil suspensions, the normal cation exchange reaction was rapid and both external and internal sites were readily accessible. Therefore in such systems limited reversibility or hysteresis was related to other causes.

Wiegner and co-workers\textsuperscript{74} studied the simultaneous release of calcium and ammonium from Ca-NH\textsubscript{4} clays prepared either by adsorption of NH\textsubscript{4} on Ca-clay or adsorption of calcium on NH\textsubscript{4}-clay, the procedure otherwise being the same. Both ammonium or calcium proved to be more difficult to replace if present initially upon the clay than if introduced later. The properties of the exchanger, therefore, seemed to be affected by the ion with which it was originally saturated. This effect of order of entry, whenever demonstrated, was always the same. Hysteresis occurred more frequently for heterovalent than for homovalent ions. Working with bentonite, Vanselow\textsuperscript{18} found strong hysteresis for Ca-NH\textsubscript{4} but none for Ba-Ca and Ba-Cu exchanges.

For ions showing hysteresis, the ion species first present on the exchanger became partly fixed and was not altogether available for exchange. High temperature and rehydration often proved to be a means of reducing or overcoming hysteresis.
Recently Maes and Cremers\textsuperscript{75} working with montmorillonite showed that cation exchange hysteresis was a pH dependent effect. They demonstrated that the extent of irreversible adsorption of Co\textsuperscript{2+} and Zn\textsuperscript{2+} ions in Na-montmorillonite depended upon the composition of the solid phase and pH. At low and intermediate occupancy of the divalent cation, the adsorption was perfectly reversible up to a pH value of about 6. At very high occupancy approaching saturation a significant portion of the adsorbed divalent cations became irreversibly fixed but could be desorbed by a pH decrease.

**PESTICIDES**

Pesticides signify any substance or mixture of substances intended for preventing, destroying, repelling or mitigating insects, mites, fungi, rodents, nematodes or weeds which may be present in any environment whatsoever. Successful use of pesticides depends to a large degree of the formulation of the preparation and the conditions under which the chemical compound is brought into contact with the pests of plants.

Pesticides are divided into various basic groups, depending on the purpose for which they are used, e.g., insecticides used for insect and mite control, herbicides for weed control, fungicides for fungus control, nematocides for nematode control etc.

Some of the important compounds used as pesticides are B.H.C., aldrin, lindane, 2,4-D, \textit{s}-triazines, diquat, paraquat, oxamyl, phosphonidon, telone, nickel chloride, calcium arsenate, cuprous oxide, methyl bromide etc.
The interaction of the pesticides with soil particles may lead to some physico-chemical changes in them causing inhibition of nitrification, an increase or decrease in CO₂ production and nutrient availability to plants. In view of the pesticidal chemicals being toxic and capable of contaminating the air, water and soil and altering their quality and thereby producing undesirable effects on man and his environment, their utilization must be done with great care and knowledge. Hence studies of the nature of interactions of pesticidal chemicals on clays and soils are important in this light.

**SURFACTANT**

Most of the physico-chemical reactions which occur in soil systems are surface reactions involving the clay fraction. By manipulating or altering the surface activity in a favourable manner the effects of adverse soil structure can be minimized or controlled. Such chemical compounds which alter the conditions prevailing at interfaces are known as surface active agents or more commonly referred to as surfactants. Some important surfactants are soaps, waterproofing agents like greases and emulsifying agents such as glue, egg white, natural gums and various other organic substances. Surface active agents also include wetting agents, emulsifiers, detergents and spreaders, sticking and dispersing agents.

Surfactants are classified into two main classes; ionic and non-ionic depending upon their ionisation or dissociation in water. The ionic surfactants are further sub-divided into anionic and cationic sub-groups. Non-ionic surfactant active agents have no particle
charge whereas ionic agents show either a positive (cationic agent) or negative charge (anionic agent). When the linear hydrophobic portion of the molecule forms the anion in aqueous solution it is said to be anionic surfactant. If the molecule ionises so that the linear hydrophobic portion forms the cation it is cationic surfactant. The non-ionic class is characterized by non-ionised, hydrophilic end-groups that are usually polar active in nature. They are classed as non-electrolytes and demonstrated to be effective when applied to water repellent soils for increasing infiltration, decreasing soil erosion and increasing seed germination\textsuperscript{77-80}.

Like pesticides, surfactants are also in wide use now days in agriculture. They are used to improve the slow infiltration in water repellent soils\textsuperscript{81,82} in many areas of the world. Several studies\textsuperscript{83-86} have revealed that surfactants and pesticidal compounds can interact with soil and clays and this interaction depends upon the pH, the particle size, the nature of the surfactant etc. and therefore it influences their adsorption and mobility in soils. The effect of two non-ionic surfactants on adsorption and mobility of lindane, diuron and atrazine was studied\textsuperscript{87} and it was observed that in the presence of high concentration of surfactants, there was a decrease in adsorption and increase in the mobility of pesticides. Bayer\textsuperscript{83} attributed the effect of surfactants on the mobility of diuron to their influence on soil physical properties.

Lack of interaction or little adsorption on clays and soils were reported for anionic surfactants\textsuperscript{88-90}. A study on adsorption
mechanism of surfactants with montmorillonite was made by Law and Kunze\textsuperscript{90}. They found that anionic surfactants were not adsorbed in appreciable quantities and had no marked effect on the d-spacing of montmorillonites and thus have no interference with the hydration of clay surface. Cationics were strongly adsorbed by the clay surface through ionic bonding in amounts equal to or even greater than the cation exchange capacities of the clay. Both cationic and non-ionic compounds were held in the interlayer space of montmorillonite and tended to form double layer if sufficient material was present.

Hower\textsuperscript{91} studied the behaviour of surfactants on clays and found that the mechanism of adsorption of cationic and non-ionic surfactants was just opposite to that of anionic surfactants. He observed that the amount of anionic surfactants adsorbed by Na-montmorillonite was significant. It was also concluded that in some instances anionic adsorption could approach that of non-ionic and cationic adsorption. Wayman\textsuperscript{92} studied the adsorption of anionic surfactants on kaolinite, illite and montmorillonite and found that the adsorption was dependent on various factors. It increased with the increase in concentration, length of alkyl chain, presence of PO\textsubscript{4}\textsuperscript{3-} and soluble chloride salts and decrease in pH of the soil system. Gaynar and Volk\textsuperscript{93} studied the surfactant effects on picloram adsorption by soils and they observed that adsorption of picloram from soils containing cationic surfactants was greater than that containing non-ionic and anionic surfactants. Low concentrations of surfactant solutions slightly increased the adsorption while high concentrations decreased the adsorption of pesticides\textsuperscript{81,87}. 
The effect of surfactants on vegetable species was studied as a field experiment by Lazzati on potato crops. The ionic surfactants increased the concentration of nitrate-N of the soil. Both the surfactants significantly inhibited dehydrogenase activity. Higher concentrations reduced the overall yield but increased the contents of ashes, proteins and K in the tubers. The weight loss of potatoes during cold storage was increased by non-ionic surfactants and reduced by the anionic one. Veloras, Letay and Osborn studied the surfactant soil interaction effects on barley growth. Less than 1% of surfactant applied to the soil was taken up and translocated in the barley plants. The effective longevity of the treatment with non-ionic surfactants and potential water pollution were affected by surfactant degradation in soil peat.

The surfactants and detergents have been found to possess powerful bacterial properties. They are used for compounding a variety of insecticidal, fungicidal and herbicidal formulations and thus they find use in soils.

**CLAY-ORGANIC REACTIONS**

There is evidence of some kind of a reaction between the fundamental components of clay and organic materials. Adsorption and fixation of humic acid and protein by clay and as a result of it, reduction in its base exchange capacity are some of the popular examples of clay-organic interactions.

Adsorption as well as ion exchange occur between montmorillonite clay and organic molecules. Reactions between montmorillonite
and organic bases and their salts, and with methylene blue were found to be of ion-exchange type. Such reactions are more common with organic cations containing basic amino groups.

It was indicated by Hendricks that the organic ions are held by van der Waals forces in addition to the coulombic force and are supplemented by C-H...O bonds between the organic molecule and the clay mineral surface. The larger ions are adsorbed more strongly and in excess because of the greater van der Waals forces whereas small ions are adsorbed only up to the cation exchange capacity.

Many non-ionic, polar organic molecules which are dipoles as a result of the lack of symmetry of electron distribution, can be adsorbed on the basal surfaces of montmorillonite because the clay mineral structures are also polar. The types of exchangeable cations are also found to affect the adsorption of pesticidal organic compounds by clays significantly.

Numerous scientists contributed to the literature on interaction of organic cations. Recently Zheng et al. and Donar and Mortland studied the interaction of some amides and substituted amides on alkyl ammonium-clays using x-ray diffraction measurements that indicated the intercalation of alkyl amide compounds causing interlayer expansion of montmorillonite.

Intermolecular H-bonding was established as an important mechanism in the adsorption and retention of neutral organic compounds like octadecylamine, pyridine, 3-amino triazole and S-triazines which become cationic after adsorption at clay surfaces.
through protonation. The sources of the protons were exchangeable 
H⁺ occupying cation exchange sites, water associated with metal cations at the exchange sites or proton transfer from another cationic species already at the clay surface. It was obvious that the existence of an organic compound in cationic or molecular form was dependent upon the acidity or proton supplying power at the clay surface. Protonation by water associated with metal cations at the exchange sites depended upon the polarizing power of the cations.

Many compounds formed symmetrical hydrogen bonding or hemisalt like complexes with clays e.g. ethyl ammonium ethyl amine-montmorillonite, pyridinium pyridine montmorillonite and urea-montmorillonite.

The adsorption of S-triazines by clays was reported to increase with the decrease in pH. Under pH conditions where the compound existed as the uncharged form adsorption was predominantly by replacement of water molecules from the clay surface. Therefore the bonding between the organic pesticide and clay was not a strong one and the adsorbed molecules could be desorbed by adding water to the system. Mortland showed by i.r. data that urea was held on to Cu(II)-, Mn(II)- and Ni(II)-montmorillonite by means of coordinate bond which occurred through carbonyl rather than amino group. I.R. studies for EPTC adsorption on clays showed that coordination of EPTC molecule to clay exchangeable cation occurred through oxygen of carbonyl group and exchangeable cation. Thus it was observed that the nature of saturating cations played a decisive role in adsorption process of polar organic molecules.
Clay organic interactions are important in nature as well as in industry. In soils organic compounds derived from plants and animal remains and their decomposition products influence the moisture and aeration properties and also affect the reactivity of the clay fraction of the soil. As the use of organic chemicals in the form of pesticide and surfactant is constantly increasing in agriculture, such studies are of great help in understanding the nature of clay-organic interactions for the safe and effective use of such organics in soil.

CHROMATOGRAPHIC TECHNIQUES USED IN THE STUDIES OF SOIL INTERACTIONS

Chromatographic methods which are quite inexpensive, sensitive, selective and rapid are finding applications in more advanced research areas. These methods of chemical separation may be classified as gas, paper, column, thin layer and ion-exchange techniques of chromatography. Chromatograms may be formed by partition, adsorption or ion-exchange or some combination of these. Different types of chromatographic techniques are based on the same principle that the components of the mixture could be separated from one another by passing it through a two phase systems, one mobile which may be liquid or gas and which is in equilibrium with a stationary phase like silica gel, soils, clays, alumina or ion exchange resins etc.

Column chromatography: It may be defined as the uniform percolation of a liquid through a column of finely divided substance. The interaction of a substance with the stationary phase may occur in
several ways. There may be direct interaction between the substance and the surface of the stationary phase or the stationary phase may merely hold a second fluid phase so that the distribution involves a partition between two liquid phases. The sample is injected at the top of the column and the solvent or mobile phase is allowed to flow through the column resulting in the movement of the sample molecules along the column and a partial separation of components. The differential migration results from the equilibrium distribution of different components between particles or stationary phase and the flowing solvent or moving phase. The differential migration is determined by the experimental variables which affect this distribution, the composition of the moving phase, the composition of the stationary phase and the separation temperature.

Column selectivity is an important factor in obtaining a desired separation. In preparation of the column we strive for maximum column efficiency and permeability. An increase in length/width ratio of the column improves column efficiency. By using smaller particle size for packing to gain higher column efficiency, we sacrifice permeability so a compromise in particle size is often made.

There are two methods of packing the column, top-fill dry packing method and the wet method. Silica gel, starch, calcium carbonate, alumina, charcoal are some commonly used adsorbents. There are simple or many modified devices for sample injection\textsuperscript{121,122}. The choice of solvent or mobile phase is all important in liquid-solid
chromatography. Solvent flow can be controlled by varying the height of the solvent level above the column or by altering the column inlet pressure.

Flow rate of the solution used as mobile phase can be adjusted by proper selection of driving pressure, column packing material, density of packing, viscosity of mobile phase and temperature. Some workers\textsuperscript{123} conclude that separation is independent of flow rate. Several devices are suggested for improved control of flow rate\textsuperscript{124,125}.

Developers are selected so that they have the affinity for adsorbent than the ions which are under examination. Fractions of the eluted liquid are collected and are identified by some appropriate method using chemical reagents or devices like photometry, polarography, densitometry, fluorimetry and radio-tracer technique etc.

If the substances are not eluted from the column, they can be removed by cutting the column in some equal portions after completion of the process. Mostly this is done in soil columns. Sometimes split tubes are used so that after completion of the experiment the wrapped cellophane tape, used to join the two lengthwise halves of the tube, is removed and the column material is exposed which can be cut at desired zones and components are extracted.

In fact a soil column provides a suitable and convenient soil bed analogue to soil profile in fields. The distribution of
organic chemicals in the soil profile after irrigation or rainfall is important because the effectiveness of a given pesticide applied to the soil is dependent in part upon its position in the soil profile. Besides this, persistent organic chemicals can build up in the surface soil if they are strongly adsorbed or can be leached into ground water if they are very mobile. Using the soil columns Huggenberger et al.\textsuperscript{126} calculated the distribution of the pesticide lindane in soil after water infiltration and also presented a model to calculate the pesticide distribution theoretically, when it was assumed that the adsorption process of lindane in soil was completely reversible. Similarly a field model\textsuperscript{127} based on a numerical solution to the flow equation was developed to provide a simple means of calculating the loss of water and its distribution in the field soil profile. For this, a column model was used which was derived on the basis of soil column-water infiltration experiment. In recent years a number of workers\textsuperscript{82,87,128-131} contributed to the literature on the distribution of various surfactants and pesticides in soil under different water flow conditions. LaFleur\textsuperscript{132-133} presented the mechanism of distribution and movement of many pesticides using soil columns. In the study of picloram displacement in soil profiles\textsuperscript{134}, soil columns were used for laboratory experiments and conclusions derived were subsequently applied to field experiments where the picloram displacement was caused by seasonal rainfall plus irrigation. Thus soil column chromatography is becoming a very convenient and useful technique in the field of soil chemistry.
Soil Thin Layer Chromatography: Soil Thin Layer Chromatography is mainly based on adsorption where the adsorbent is a thin layer of soil deposited on a glass plate. Soil components provide an adsorptive phase where adsorption and desorption take place very rapidly and reversibly. Constituents like soil organic matter further increase the adsorptive property of the soil layer. This and ion-exchange property make the soil more effective as a static phase in soil TLC.

Thin layers are prepared by spreading a uniform film of a slurry of the soil adsorbent. Normally the liquid portion of slurry is water which may also contain acids, bases, buffers or other complexing agents. Though the thickness of the layer does not affect the diagnostic or qualitative work but better results are obtained if the layers are thin because the spray reagent is much more sensitive with it. The amount of substance applied depends upon the layer thickness and the visualization procedure which are inversely proportional to each other and also on the nature of adsorbent and type of chromatography viz. adsorption or partition.

The sample is placed or spotted about 2.0 cm or 1 inch from the end of the plate so that the solvent level will be at least 1 cm below the centre of the spot. Plates containing the sample on a bound thin layer are developed by placing them in a vertical position of a closed saturated system such that the bottom of the layer dips into the developing solvent. Usually in addition to the chemical reagents used as detectors to locate the separated components on the
chromatogram, other methods are also used. Helling used radioactive carbon in the applied pesticidal chemicals and after development, the movement of pesticides was detected by radioactive scanning. The height of the chromatogram is dependent upon the adsorption affinity of the corresponding component and the width is proportional to the quantity of the loaded substance. $R_F$ is defined as the ratio of the distance travelled from the starting point by the substance to the distance travelled by the solvent front. A knowledge of the properties of adsorbents and the nature of the forces responsible for adsorption is essential. In polar adsorbents ion-dipole and dipole-dipole interactions play a major part in the movement of the substance and capillary action. Movement of fluid is also controlled by particle size in soil TLC.

In 1968, Helling and Turner first used thin layer chromatography for the detection of pesticides in soils by applying soil thin layers on glass plates. In 1970, Rhodes, Belasco and Pease used soil TLC for determination of agrichemicals like monuron, diuron, bromacil, terbacil and chloronels in soil by measurement of $R_F$ values where the chromatograms were developed in water. Chapman, Gabbot and Osgerby used the soil TLC for measuring the relative movement of herbicides in soil. Inch and his coworkers used this technique for determining the mobility of some insecticides. Helling further extended this work on soil TLC to study the mobility of a large variety of pesticides and concluded that adsorption is the predominant factor that influences pesticide movement. Some other workers also used this technique to
study the mobility of trace elements under different soil conditions. Recently Singhal and co-workers\(^{138-140}\) used soil TLC to study the movement of some pesticides and amino acids. All these studies mentioned above show very clearly that movement of substances or their separation can be affected by altering the conditions of the static phase, developer and of the applied substances. In recent years, a number of soil chemists have used this technique for the separation and identification of a large number of herbicides, insecticides and nematocides by making alterations in adsorbent phase and in solvent phase. In 1976 Chakrabarti and Roy\(^{141}\) generalised a procedure for separation and identification of pesticides by TLC in which sixteen pesticides belonging to different groups were separated over natural alumina coated plates using petroleum ether-dioxane-liquid paraffin as solvent phase. Krasnykh\(^{142}\), in 1977, determined heptophos (a nematocide) in water, soil, potatoes, and cucumber by TLC using silica gel as stationary phase and a mixture of benzene and chloroform as the mobile phase and n-hexane as the extractant. Tewari and Harpalani\(^{143}\) used this technique for the determination of organo-phosphorous insecticides in tissues. Gupta and Dewan\(^{144}\) estimated carbofuran and 3 ketofurans in plants, grains and soils by TLC with the comparison of their spot sizes with the spot of standard one.

Thus the technique of soil TLC is now in wide use for various other studies with soils and clays of diverse nature and it opens a wide new field of research for soil scientists. It provides a very large field of application for investigating problems
in various applied and non-applied fields.

THE PROBLEM

Interaction of pesticidal and surface active organic chemicals in soils has been a subject of studies in recent years and a great deal of attention has been given to this work. Phosphorus containing organic compounds are of great importance in biological systems. Organo-phosphorus insecticides are becoming much popular in agriculture. Phosphomidon, a vinyl phosphate insecticide \([0,0,\text{dimethyl},0 (\text{1-methyl}, 2-\text{chloro}-2-\text{diethyl carbamoyl-vinyl})\text{phosphate}]\) has shown a broad spectrum against certain forest and insect pests of field crops like cotton, fruits and vegetables and also for some ornamental plant pests though in some instances it has demonstrated a certain degree of specificity. Dimecron is a commercial formulation of phosphomidon which is coloured violet due to incorporation of some dye for the purpose of safety.

Metabolism of phosphomidon in plants and animals and the nature of metabolites have been studied by some workers but no attention has been paid to the mode of interaction of this pesticide with clays and soils. It was therefore considered worthwhile to examine the mechanism of the interaction of Dimecron with standard clays with the help of adsorption isotherms, thermodynamic parameters, x-ray and infra-red techniques to reach some useful conclusions.

Besides the use of organic agrichemicals, inorganic trace-elements which are taken up as plant nutrients from soils are
also considered essential for healthy development of animals, plants and microorganism. Mobility of such inorganic substances placed onto or within the soil which may influence their availability, effectiveness or potentiality, is largely controlled by adsorptive and ion-exchange behaviour of soils and clays. In view of the importance of the subject in plant nutrition it was considered that such a study on ion exchange behaviour of clays and also mobility of trace elements in soils will be useful. Simple and convenient techniques of soil TLC and soil column chromatography were used in these investigations.

The subject matter of the thesis entitled "Physico-chemical studies on clays and soils" has been given in five chapters on the following plan:

CHAPTER I

Adsorption and interaction of Dimecron \([0,0\text{-dimethyl},0\text{-methyl-2-chloro-2-diethyl carbomoyl-vinyl}}\text{ phosphate}] with acid and base saturated montmorillonites.

CHAPTER II

Thermodynamics and mechanism of adsorption of Dimecron on acid and base saturated montmorillonites.

CHAPTER III

The effect of cetyl pyridinium chloride and sodium lauryl
sulphate on adsorption and mobility of Dimecron on illitic Aligarh soil.

CHAPTER IV

Influence of salinity, alkalinity, phosphate and organic matter on mobility of trace elements in soils.

CHAPTER V

Hysteresis and reversibility in calcium-ammonium exchange in bentonite.
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