CHAPTER 1

INTRODUCTION
1.1 Introduction

Intercalation chemistry of layered clays has grown into a wide field of research (1-4). The vast array of materials that can be tailor made for varied applications is the basis of this growing interest. Extensive studies have been made to understand sorption properties of clays (5-10). Adsorption of heavy metal ions, radioactive wastes and hazardous gases are among the important studies (11-14). Another attractive application of clay based materials is catalysis in organic synthesis. Different types of pillared interlayered clays [PILC], metal ion exchanged and acid treated clays are studied by many workers (1-3, 15-18). Intercalated clays find use as chemical sensors, enantiomeric separators, bioactive materials and slow release supports for pesticides, drugs etc. (19-24). Smectite group of clays, particularly montmorillonite clay (Mnt hereafter), is widely used for such studies because of its versatile nature (25).

1.2 What is clay

Scientifically, clays are termed as “a natural, earthy, fine grained material which is composed largely of hydrous aluminium and magnesium silicates”. The -2μm grain size is the upper limit for clay minerals. The layer silicates contain continuous two-dimensional tetrahedral sheets where individual tetrahedra are linked with each other by sharing of three basal oxygens. The fourth oxygen, i.e. the apical oxygen points in a direction normal to the sheet and simultaneously links an adjacent alumina octahedral
sheet in which the individual octahedra are bound by lateral sharing of octahedral edges. The smallest structural unit contains three octahedra. If all three octahedra are occupied, the sheet is classified as trioctahedral. If only two of the three octahedra are occupied, it is classified as dioctahedral. The octahedral cations are Mg$^{2+}$, Al$^{3+}$, Fe$^{2+}$, Fe$^{3+}$ and also Li$^+$, Ti$^{4+}$ etc. The tetrahedral cations are normally Si$^{4+}$, Al$^{3+}$ or Fe$^{3+}$ (26).

1.2.1 Classification of clays

Of the main groups of clay minerals, the 1:1 types are formed by linking one tetrahedral sheet with one octahedral sheet. Here, the uppermost unshared plane of anions in the octahedral sheet consists entirely of OH' groups. The 2:1 type is formed by linking two tetrahedral sheets with one octahedral sheet in between. The upper tetrahedral sheet is inverted so that the apical oxygen can be shared with the octahedral sheet. Both octahedral anion layers are then of O, OH composition. In 2:1:1 clays, two negatively charged 2:1 layers sandwich a positively charged brucite layer (Fig.1.1 & Fig.1.2).

1.2.2 Cation Exchange

Cation exchange capacity (CEC) is the quantity of cations reversibly adsorbed per unit weight of mineral expressed in terms of meq/100gm of clay. In smectites the cation exchange capacity results from substitutions in the lattice structure. The predominant substitutions are Mg$^{2+}$ and Fe$^{3+}$ for Al$^{3+}$ in the octahedral sheet, but Al$^{3+}$ may be substituted for Si$^{4+}$ in the tetrahedral sheet.
Fig. 1.1 Diagrammatic projection of the structures of clay minerals. (a) 1:1; (b) 2:1; (c) 2:1:1

Silicon • Aluminium or Magnesium ○ Oxygen ○ Hydroxyl group
Fig. 1.2 (a) Schematic illustration of the crystal structure of triotahedral 2:1 phyllosilicates showing the basal spacing in the c-axis; (b) Tetrahedral sheet viewed perpendicular to the silicate layer
Table: 1 Classification scheme for phyllosilicates related to clay minerals

<table>
<thead>
<tr>
<th>Type</th>
<th>Charge/ formula unit</th>
<th>Group</th>
<th>Sub group</th>
<th>Common species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>~0</td>
<td>Kaolinite-</td>
<td>Dioctahedral</td>
<td>Kaolinite</td>
</tr>
<tr>
<td></td>
<td>Serpentine</td>
<td>Trioctahedral</td>
<td>Serpentine</td>
<td>Antigorite</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>~0</td>
<td>Pyrophyllite-</td>
<td>Dioctahedral</td>
<td>Pyrophyllite</td>
</tr>
<tr>
<td></td>
<td>Talc</td>
<td>Trioctahedral</td>
<td>Talc</td>
<td>Talc</td>
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<td></td>
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<tr>
<td></td>
<td>~0.25-0.6</td>
<td>Smectite or</td>
<td>Dioctahedral</td>
<td>Montmorillonite</td>
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<td></td>
<td>Montmorillonite-</td>
<td>Trioctahedral</td>
<td>Saponite</td>
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<td></td>
<td>Saponite</td>
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<tr>
<td></td>
<td>~0.6-0.9</td>
<td>Vermiculite</td>
<td>Dioctahedral</td>
<td>Dicicahedral - Vermiculite</td>
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<tr>
<td></td>
<td></td>
<td>Trioctahedral</td>
<td>Vermiculite</td>
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<td></td>
</tr>
<tr>
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<td>Mica</td>
<td>Dioctahedral</td>
<td>Muscovite</td>
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<td></td>
<td></td>
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<td>Mica</td>
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<td></td>
<td></td>
<td>Biotite</td>
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<td></td>
<td>~2</td>
<td>Brittle mica</td>
<td>Dioctahedral</td>
<td>Margarite</td>
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<tr>
<td></td>
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<td>Trioctahedral</td>
<td>Brittle mica</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2:1:1</td>
<td>variable</td>
<td>Chlorite</td>
<td>Dioctahedral</td>
<td>Donbassite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Di,Triocahedral</td>
<td>Chlorite</td>
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<td></td>
<td></td>
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<td>Chlorite</td>
<td>Sudoite</td>
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<td></td>
<td></td>
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<td>Pennine</td>
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This gives rise to charge deficiency which varies depending on the degree of substitution. These charges are sometimes balanced by other lattice arrangements e.g. replacing OH for O or by filling more than two thirds of the possible octahedral positions. But frequently these charges are balanced by external alkali (Na) or alkaline earth (Ca) metal ions. These cations are found to be mostly on basal cleavage surfaces of the clay minerals. In most of the clay minerals the CEC results from substitution in the octahedral sheet. When the substitution is in the tetrahedral sheet the exchangeable ion are held more strongly than the substitution in the octahedral sheet. For example, in mica the interlayer potassium ions are held so strongly that they are almost fixed in the interlayer space. Incorporation of a guest species into the clay interlayer is depicted by the term intercalation or intersalation. When a cationic species is exchanged into the interlayer of a clay up to the CEC it is termed intercalation and when the exchange is excess over the CEC it is termed intersalation.

1:1 layer silicates, which are also termed as Kaolinite-Serpentine group includes the dioctahedral mineral kaolinite. Here the layers are held together rather firmly by hydrogen bonding between OH⁻ groups of one layer and O²⁻ ions of the adjacent layer. Kaolinites posses a low cation exchange capacity of 3-15 meq/100gm and the major source of exchangeable cations is the broken edges of the silica-alumina units. 2:1 clays have high CEC (70–130 meq/100mg) and swell extensively in water. 2:1:1 clays have low CEC and do not swell at all in water and exchangeable cations exists on external and edge surfaces.
1.2.3 Surface area and CEC

In most of the layer silicate clays, surface area and CEC are directly proportional to the structural charge. As in case of kaolinite for a low structural charge the surface area is 5 –20 m²/gm and CEC is 3-15 meq/100 gm. Micas are an exception as they have very high structural charge yet the surface area and CEC are low. It is because of the K⁺ ions in the interlayer region, which prevent solvation or cation exchange (28).

1.2.4 Anion exchange

Another type of exchange process also takes place in layer silicate clays which is anion exchange. The amount of exchanged anion is expressed as anion exchange capacity (AEC).

Anion exchange is possible by replacement of OH⁻ ion, as has been suggested by many authors for phosphate adsorption by kaolinite. The extent of replacement depends on the accessibility of OH⁻ groups. Anions like phosphate, arsenate and borate which posses same size and geometry as the silicate tetrahedra may be adsorbed by fitting to the sheets as extensions. On the other hand, sulphate, chloride and nitrate ions cannot be adsorbed as their geometry does not match with the silica tetrahedral sheets. In another way it is suggested that there may be excess positive charge because of breaking of an alumina bond (20) at the edge as -

\[ -\text{Al} - \text{O} - \text{Al} - \xrightarrow{\text{H}_2\text{O}, \text{H}^+} 2 (-\text{Al} - \text{OH}_2^+) \]
1.2.5 Ion dipole interaction

Ion dipole interaction occurs in case of adsorption of polar neutral molecules e.g. organic compounds like ethylene glycol. The negative charge of the clay layer or the interlayer cations may act as the polarizer.

1.2.6 Coordination mechanism

Intercalation occurs through coordination mechanism also. A metal ion in an interlayer space may provide a coordination site for an intercalated molecule. Alcohols, glycols, amines, amides and nitrites (6,10,28) are some examples of such molecules.

1.2.7 Swelling

Swelling is the most prominent property of smectite type clays (Fig.1.3). It is the ability to expand beyond a single molecular layer of intercalant. Extent of swelling depends on the polarity of the swelling agent, the interlayer cations, the layer charge and the location of the layer charge. When water penetrates the interlayer forming one to four monolayer, the volume of the dry clay just doubles, then this swelling is termed as interlayer or intracrystalline swelling. When the moisture uptake goes beyond this, and a spectacular swelling occurs along with water adsorption on external surfaces and pores also, it is called osmotic or intercrystalline swelling (30).
Fig. 1.3. Schematic presentation of swelling of smectite clay in presence of water.
With different polar solvents, the basal spacing of a clay becomes different, e. g. for ethylene glycol the Na-Mnt has a basal spacing of 16.9–17.1Å, for glycerol it is 17.8Å while for water it may be indefinite.

The interlayer cations influence the swelling nature of clays. As the different cations have different polarizing power, same solvent will give different basal spacing for a clay. Thus, for water (at 52% relative humidity) Na-Mnt exhibits a basal spacing of 12.5Å, NH₄-Mnt–11.7Å and Ca-Mnt 15.1Å (25).

Layer charge is another factor which influences the swelling of clays. Na- and Li-Mnt are two of the most swellable clays. In illite the layer charge is high and the location of charge is in tetrahedral sheet, obviously, the interlayer cations and also the adjacent layer experience a strong force. Thus water or any other solvent hardly penetrates into illite interlayer. On the other hand, the layer charge in Mnt is low and location of the charge is in the octahedral sheet. Here, the interlayer cations experience a uniform force which is obviously weaker than illite. Thus, solvation in Mnt is easy. In fact, it is the most swellable clay in Na-exchanged form. In water it delaminates completely.

1.2.8. Structure of clay in water

Structure of clay minerals in water is in general affected by the strong likelihood that the edge surfaces may acquire a positive charge while the flat surfaces posses a permanent negative charge. Hence, in solution a platy clay mineral may have a positive double layer on the edge surfaces and a negative
double layer at the same time on the flat surface. Because of this the clay suspension behaves in a complex manner. Thus, on flocculation clay platelets may associate in an edge-to-face, face-to-face or edge-to-edge arrangement (Fig. 1.4) depending on the complex balance between the attractive and repulsive forces involved (30). Gelation is a special type of flocculation. In Mnt, gelation occurs at a concentration as low as 2% clay by weight. With increasing concentration it increases. Gelation results from layer edge-to-face interactions which generate a "House of cards" structure (29, 30).

1.2.9. Mechanism of hydration

Mechanism of hydration is studied by a number of workers (31-34). It is seen that the first molecules of water taken up on the surface of a clay mineral are strongly held. The force of attraction may result from hydrogen bonding between the water molecules and the oxygen atoms of the surface. Bonding may also occur between water molecules and surface hydroxyls. IR spectroscopic studies on smectite show that the first stage of water adsorption by these clays is the solvation of the exchangeable cations by either three (monovalent cations) or more (bivalent cations) water molecules. These hydration states correspond to interlamellar c-axis spacings large enough to accommodate one or more layers of adsorbed water molecules. The second stage of hydration involves formation of an octahedral solvant complex for the monovalent cation or a second solvation sheath for a divalent cation. This depends on the ability of exchangeable cation to solvate. This may not
Fig. 1.4. Particle-particle association of clay platelets in a clay suspension in different edge to edge, edge to face and face to face aggregated /flocculated systems.
necessarily lead to formation of complete monolayers of water in the interlamellar space. The extent to which the internal surface is hydrated depends on the solvation energy of the cation. The hydration of smectites beyond the solvation of cations results in condensation of water in micro-pores and on external surfaces.

Beyond the first few monolayers of water on clay mineral surface, uptake of the water is in accordance to a concentration gradient. This is because there are more ions per unit volume of solution in the vicinity of a clay mineral surface than in the bulk of the solution. On hydration the concentration of the double layer solution becomes more like the concentration outside it. If the pore concentration is greater, swelling due to this mechanism is likely to be limited. Here, the hydration is controlled by osmosis. Hydration up to the first few monolayers is influenced by chemical and ion-hydration effects. While the uptake of water at distances greater than 10Å from the surface probably involve osmotic or Donnan equilibrium type processes (29).

Some important results are obtained from ESR studies on structure of water adsorbed near Cu$^{2+}$ ions in smectites (34). Here, it is shown that a symmetry axis approximately perpendicular to the silicate surfaces passes through the tetragonal solvation complex, Cu(H$_2$O)$_4^{2+}$. The water molecules near bivalent exchangeable cations are well organized at low water contents in a manner consistent with ion size and the neighbouring silicate layers. As the
water content increases, the hydrated cations behave more like that of a cation in an aqueous solution which is known as tumbling.

1.2.10 Forces acting in interlayer of clay

The forces acting in the interlayer of 2:1 type clay are computed (29). These are short range electrostatic interactions and also van der Waals attraction energy.

When diffused double layers have not been developed in the interlamellar space, the interlayer balancing cations may either occupy midway position between layers or they may be segregated and get associated with silica sheets. The force is attractive when the cations occupy midway position, and repulsive when they segregate.

The repulsive force is computed by taking the cations as dipoles with centers in the interior of the layers, each being a square plate with one centimetre edge. The net repulsion at the most likely plate sizes (1,000; 10,000Å) is rather low i.e., <0.01 mJ/m² (erg/cm²). Similarly, the attractive force is computed by supposing that the total assembly of two negatively charged layers and a layer of cations midway between the layers is a condensor. Hence the change of attractive energy $\Delta E$ with a change in interlayer spacing $\Delta x = 2.6\ \text{Å}$ accompanying the removal of one water layer is given by

$$E = \frac{2\pi\sigma^2\Delta x}{\varepsilon}$$
For a dielectric constant $\varepsilon$ of $6$ and a charge density $\sigma$ of $4.5 \times 10^4$ esu/cm$^2$, $\Delta E$ amounts to about $30$ mJ/m$^2$ (erg/cm$^2$).

The van der Waals attraction energy between two layers of a 2:1 type clay is computed according to the following formulae:

$$V_A = - \frac{A}{48 \pi} \left\{ \frac{1}{d^2} + \frac{1}{(d+\Delta)^2} - \frac{2}{(d+\Delta/2)^2} \right\}$$

In which $d$ is the distance between the plates measured between the planes of the centers of the oxygen atoms of the tetrahedral sheet and $\Delta$ is the thickness of the unit layers measured between the same planes ($\Delta = 6.60 \, \text{Å}$). The value of the constant $A$ is about $10^{-12}$ (29).

1.2.11 Exchange of cations on clays

Exchange of cations are found to be controlled by electrostatic forces. The general observation is that, when two ions of different valencies are present, the one with higher valence state is adsorbed preferentially i.e., the order is $M^{3+} > M^{2+} > M^+$ (27).

$$H^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$$

Thermodynamics studies reveal otherwise as given below: “The spontaneous exchange of low charge cations on clays is an endothermic process”.

This is confirmed by data for exchange reactions on smectites – $\text{NH}_4^+$ or $K^+$ exchange by divalent cations is driven by an increase in entropy, not by an energy decrease in the clay solution exchange system. The exchange process in clay is ruled by the van’t Hoff’s equation.
\[
\frac{d\ln K}{dt} = \frac{H^0}{RT^2}
\]

(where, \( K \) = equilibrium constant of exchange, \( H_0 \) = enthalpy, \( R \) = constant, \( T \) = absolute temperature)

i.e. as the temperature is raised, the equilibrium shifts in favor of adsorption of higher charge cations. This endothermic nature is confirmed by direct measurement of heat release or uptake during exchange.

The entropy increase could be due to increased disorder of either of the cations or water molecules during the exchange process. This entropy factor in exchange process is reasoned by the geometry of multivalent cations arranged at the layer silicate clay surface. In the Fig. 1.5(a) the possible arrangement of \( \text{Ca}^{2+} \) and \( \text{Na}^+ \) ion on a single clay platelet is shown schematically. The \( \text{Na}^+ \) ion can approach the charge sites closely but the \( \text{Ca}^{2+} \) ions cannot do so because of their strongly held hydration shells, and also because of the 10-15Å separation between the charge sites in smectites. Thus, from electrostatic bonding energy consideration, \( \text{Na} \)-clay is more stable than the \( \text{Ca} \)-clay and this explains the endothermic nature of \( \text{Na}^+ \) exchange by \( \text{Ca}^{2+} \).

**1.2.12 Active sites in clay**

Interactions of different cationic or polar species with clay surfaces may occur through a number of active sites which are identified as –
Fig. 1.5 Schematic diagram of monovalent (Na\(^+\)) and divalent (Ca\(^{2+}\)) cations retained electrostatically on a smectite with octahedral layer showing (a) a single platelet edge-on and (b) two platelets edge-on, forming interlayer region
(a) Lewis acid sites i.e. electron pair accepting sites - these occur in absence of water at surfaces such as incompletely coordinated Al e.g. tetrahedrally coordinated Al atoms resulting from dehydration of edge sites. On hydration these sites are converted to Brönsted acid sites.

(b) Brönsted acid sites i.e. proton donor sites - these occur in acid treated clays and also in clays where the interlayer cations are hydrated to a certain degree. The nature of the cation and its position - whether it is inside or outside the tetrahedral hole - influences the polarization of water and also the availability of proton. The acid strength decreases with increase of water content.

(c) Oxidizing sites i.e. electron accepting sites and

(d) Reducing sites i.e. electron donor sites - these two sites are related to Fe$^{3+}$ and Fe$^{2+}$ ions in octahedral positions and can effect reaction on both edge and face surfaces.

(e) Surface hydroxyl groups- these occur at crystal edges bound to Si, Al or other edge-exposed octahedral ions.

1.2.13 Clays in different modified forms

Clays such as smectites, vermiculites etc., are modified into various forms for different purposes. The following are some of commonly studied forms:

(a) Metal ion and metal-complex exchanged clays

Different metal ions and important metal complex cations are exchanged onto clay interlayers (3,18,36-40).
(b) Pillared interlayered clays (PILC)

These are synthesized by introducing oligomeric hydroxy metal cations (Al, Cr, Zn etc.) into clay interlayer space and calcined to generate thermally stable pillars (2,41-44).

(c) Organo clays

These are synthesized by introducing alkylammonium salts, organic cations, polymers or polar organic compounds into the interlayer space of clay imparting an organophillic character to the clay. (45-48)

(d) Acid activated clays and clays impregnated with salts

These are obtained by treating the original clays with acids such as HCl or H$_2$SO$_4$ which leads to dissolution of octahedral alumina and interlayer cations with an increase of pore volume, pore diameter and surface area but decrease/elimination of shape selectivity and framework porosity (49-58). Sometimes acid clays are impregnated with active salts such as ZnCl$_2$, FeCl$_3$ etc (59-61).

1.2.14 Clay supported catalysts

Importance of clay supported catalysts has been realized about more than forty years ago when metal ion exchanged clays were used in acid-catalyzed reactions (61). Presently innumerable organic reactions are catalyzed by clay supported catalysts in different forms (54,60-69). The following reactions are some of such examples:
(a) Friedel–Crafts Alkylation and acylation

In Friedel–Crafts alkylation various transition metal ion-exchanged clays e.g. Zn-Mnt are used (50,59). In benzylation of benzene ZnCl₂ supported Mnt K 10 (acid treated) clay is found to work very efficiently. It is found that acid activated and metal ion exchanged clay (Al³⁺, Fe²⁺ etc.) performed better in such alkylation reactions compared to even pillared interlayered clays like Al-PILC. In many cases clay catalysts are found to be more selective compared to zeolites. As for example, zeolite (ZSM-5) converted toluene to α-xylene at a rate of 25.6%, while the selectivity is 25.5%; on the other hand, pillared Mnt converted at a rate of 11.6% with a high selectivity of 43.2% towards p-xylene.

In Friedel–Crafts acylation, the clay supported catalysts are found to be very active but less shape selective.

(b) Cyclization and Diels-Alder reaction

Cyclization of carboxylic acids and diols are also catalyzed by acid clays. Dicarboxylic acids can be cyclodehydrated to give anhydrides by using an Al-Mnt and a bulk solvent (51)

Clay supported Fe³⁺ has been found to be better catalyst in Diels-Elder reaction (61).

(c) Elimination

Ion exchanged Mnt(Al³⁺, Cr³⁺, Ca²⁺) are used as catalysts for many elimination reactions as primary to secondary amine transformation, alcohol
dehydration, elimination of H$_2$S from thiols and elimination of acetic acid from acetoxypyrrole (38-40).

(d) Addition

A simple addition reaction catalyzed by Cu-Mnt is given below

\[
2RHC = CH_2 \xrightarrow{\text{Cu-Mnt}} \begin{array}{c}
\text{R} \\
\text{O} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{H}
\end{array} + \begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{R} \\
\text{O} \\
\text{H}
\end{array}
\]

Al$^{3+}$ and Fe$^{3+}$-exchanged Mnt can also be used in such addition reaction (36)

(e) Oxidation

In oxidation reactions Cr, V, Ti-pillared clays are used successfully where the active sites i.e. Cr, V, Ti ions are incorporated into the pillars. These PILCs are shape selective with an interlamellar spacing of 10–20Å and find good use in epoxidation (56).

(f) Hydrogenation and isomerisation

Catalysis of hydrogenation reaction by clay supported transition metal complexes is a good example of improved selectivity of these catalysts compared to homogeneous systems (66). The surface chemical effects influence the specificity of the catalyst, particularly when two or more pathways exist e.g. in the hydrogenation of terminal olefins with Rh(PPh$_3$)$_2$$^+$ as a catalyst precursor. In this reaction a protonic equilibrium exists between a metal dihydride and monohydride formed from the catalysts (64)
\[
\text{Rh(PPh}_3\text{)}_2^+ + \text{H}_2 \rightarrow \text{RhH}_2\text{(PPh}_3\text{)}_2^+ \rightarrow \text{RhH(PPh}_3\text{)}_2 + \text{H}^+
\]

Thus an olefin, e.g., say, 1-hexene, when adds to the dihydride, hydrogenation reaction occurs and when it adds to the monohydride, isomerization reaction proceeds. In homogeneous system both pathways operate almost in the same way with hexane:hexane ratio equal to 65:35, but when the catalyst is intercalated, the dihydride i.e., hydrogenation pathway is favoured (68).

(g) Heavy oil cracking

Heavy oil cracking is an area where pillared interlayered clays find use as Fluid cracking catalysts (FCC). PILC are better FC catalyst because of larger pore size compared to zeolites. But at high temperature coking occurs in clay supported catalysts which makes it irreversible. Moreover, the hydroxy pillars become unstable at high temperature (2, 69-71).

1.3. Clay organic interaction

Recent studies revealed that pillared clays even crudely prepared are able to retain efficiently hazardous chemicals such as dioxin(72,73). In a specific clay environment, degradation of pesticides and different chemical compounds have been reported (6, 22). The organo clay complexes may be classified into four categories (74):

(1) Intercalated organic cations
(2) Intercalated polar organic molecules
(3) Clay polymer intercalation complexes
1.3.1 Clay and amines

Some early workers extensively studied exchange of amines on clay (6). Most of the amines are exchanged as cations while some uncharged amines are intercalated after transformation to cations by surface protonation or ion-dipole interaction. Aliphatic amines prefer parallel orientation depending on the amount of amine present. The long chain amines like n-decylamine tends to be adsorbed in excess of cation exchange capacity of the clay – the excess being adsorbed as free amines due to some van der Waals interaction or H–bonding or ion–hydration.

1.3.2 Clay and alkylammonium ion

Study of intercalation of different alkylammonium ions from small to large molecular weight, has itself grown into a separate field (75, 76). Exchange of alkylammonium ions on clays was found to be linearly related to molecular weight with the exception of the smaller methylammonium and larger quaternary ammonium ions (77-80). Most of the alkylammonium clay complexes find use as sorptive materials for toxic organic compounds, often from waste water (81, 82). Clays are transformed into more hydrophobic form by treating with larger hydrophobic organic cations like dioctadecyldimethyl and hexadecylmethyl-ammonium cations. The adsorption of pentachlorophenol from waste water is observed for these organo-clay composites. On the other hand, smectites saturated with small hydrophobic
organic cations like trimethyl ammonium ions are found to be effective adsorbants for aromatic hydrocarbons from water (83, 84).

1.3.3 Clay - pesticides and herbicides

Organo clays are also important as carriers of organic pesticides and herbicides (85-88). In a study of interactions of thioamides with homoionic(Al- and Ca-)Mnt, it is seen that thiobenzamide is adsorbed through a coordination bond between the C=S group and the exchangeable cation on Al-Mnt while at the same time a small fraction is decomposed to the benzoic acid, NH₃ and H₂S. Similar study on pesticides like diazinon consisted of encapsulation via complexation with metals in the interlamellar spacing of Mnt (22). In this study it was found that intercalated pesticides were released in small amounts over a period of 7-8 weeks compared to adsorbed pesticides on Mnt which leached out within 24 hours.

1.3.4 Clay–Drug adducts

Sustained release of drugs is found to be a potential direction in the study of clay supported compounds. Interaction of hydralazine hydrochloride, a cardiovascular drug with montmorillonite was studied thoroughly in varying solution pH. The 'in vitro' adsorption of the drug along with maximum adsorption capacity and mechanism of intercalation was also considered (24).

Similar study was done for interaction of propanolol chlorhydrate with Mnt. Sustained release conforming with these were also observed for
amphetamine sulphate-Mnt (89), Clindamycin and tetracycline Mnt systems (90).

Methyl cinnamate is one of the most common component of solar filters. When incorporated into Mnt either by melting or grinding, it may form a shelter against UV 'C' radiation (91). N-methyl 8-hydroxy quinoline methyl sulphate which absorbs erymathogenic 'near UV-radiation' is also studied as smectite supported compound (83, 92).

1.3.5 Clay and other organic compounds

Adsorption and desorption mechanism of different organic compounds such as tetrahydrofuran, tetrahydropyran, dioxane, morpholine, piperidine etc., are studied elaborately (94, 95). Intercalation of methacrylamide into hydrophilic Mnt [Na- and Ca-] and organophillic Mnt [alkyl ammonium-] from different solvents was found to be dependent on the interlayer cation and the polarity of solvent used (96). Interaction of amino acids such as asparatic acid with Ca-Mnt was found to occur by formation of an outer-sphere complex with the exchangeable Ca through a ‘water bridge’ and a H-bonding of the protonated amino groups to the structural oxygen of the siloxane surfaces (97). It has been found that uptake of Cu²⁺ by Ca-Mnt is influenced by presence of organic ligands like ethylenediamine and β-alanine (98).
1.4. Inorgano-organo clays [IOC]

In a recent study, inorgano-organo clays are found to be better adsorbents for organic pollutants like benzo(a)pyrene and chlorophenols (99, 100). In this study, Mnt is modified to inorgano-organo (IOC) clay by equilibrating hydroxy Al-Mnt with cetyl pyridinium chloride. Hydroxy alumina pillared Mnt adsorbs hydrophobic pollutant like dioxins (73) and pentachlorophenols (101, 102). Yariv and co-workers (5, 103) studied adsorption of a range of organic compounds like acridine, methyl orange, crystal violet, aniline etc. on Mnt. Two types of organic interlayer cation bonding and configuration are suggested, i.e. directly coordinated and free molecules. Anilines coordinate with the clay either through water molecules or directly. The amines displace most of the interlayer water but still, even after prolonged exposure to organic liquid followed by heating at 100°C in vacuo, some interlayer water remain coordinated to cations. The coordinated amines influence the unbound amines. Within the same interlayer space different coordination complexes exist as indicated by integral basal spacing.

1.4.1 Clay-polymer composites

Intercalation of polymer (e.g. polyethylene oxide) into homoionic phyllosilicates like Mnt and hectorite give rise to another composite material with good chemical and thermal stability besides preserving the ion-exchange properties (104). Moreover, an enhancement of electrical conductivity due to interlayer cations with respect to the parent silicate is observed.
1.4.2 Adsorption of toxic gases and heavy metals

Toxic gases and heavy metals pose a big ecological risk as very toxic contaminants. It is found that clay in different modified forms successfully adsorb these pollutants.

A number of Japanese patents are on adsorption of toxic gases like mercaptane, sulphides, ammonia and amines etc. Deodorants (105) based on swellable mica layers exchanged with potent metal ions like Fe, Ni and Zn are found to be effective in removing ammonia and organic amine. In another invention (106) deodorants are prepared by loading metal ions of Cu, Co, Cd, Ag, Zn etc., on smectite which are efficient in arresting H₂S from air.

Adsorption of heavy metals by clay and modified clay is studied extensively by different workers. A comparative adsorption of heavy metals like Cu, Zn, Pb, Cd etc. by Ca-Mnt, Al-hydroxide and clay-Al-hydroxide systems from aqueous suspension are discussed (107). Similarly, adsorption of Co²⁺ and Cd²⁺ on Wyoming Mnt was studied as a function of salt concentration (NaCl and NaNO₃), adsorbate concentration, pH and presence of complexing ions (108). Zn²⁺ and Pb²⁺ are often found as major contaminants of effluent water. When salt solution of these two metals in different ionic strength are allowed to interact with Mnt, Zn²⁺ was found to exchange more easily than Pb²⁺ (109). Competitive sorption of phosphate and oxalate on an Al(OH)ₓ–Mnt was found to be influenced by pH, order of anion addition and initial oxalate/phosphate molar ratio (110).
1.4.3 Bioactivity of clay supported compounds

Bioactive materials when intercalated or supported on clays show improved activity and thermal stability. Silver chelate of 2-(4-thiazolyl)-benzimidazole intercalated into Mnt showed strong anti-fungal activity up to 200°C and even after decomposition at 400°C, the resulting Ag-clay was found to be active to fungi. This clay composite was stable to sunshine for several weeks (111). In another study silver chelate of hypoxanthine intercalated in Mnt was found to be bioactive (112). Some ammonium cations are found to have strong anti-microbial and anti-fungal activity, e. g. benzalkonium chloride, didecyldimethyl ammonium, cetyltrimethylammonium chloride etc. These cations are intercalated and evaluated as thermostable (~250°C) bioactive agents (113). Such thermostable supported anti-fungal and antimicrobial materials are useful as ceramic filter or coating (114, 115).

1.4.4 Biomimetic catalysts

Clay supported biomimetic catalysts are a new development in this area. When metalloporphyrins {like Fe(III) or Mn (III) porphyrins} are intercalated into clay layers, they mimic the natural heme-protein, cytochrome P-450. This heme-protein plays a key role in catalyzing oxidation reactions involved in biosynthesis and biodegradation of hormones, fatty acids and metabolism of drugs etc., (116). In case of the model clay supported catalyst also organic syntheses were found to occur in a similar way.
1.4.5 Clay supported chemical sensors

Expanded or pillared clays can be used to synthesize selectively sensitive luminescent micro-porous films which can be potential chemical sensors (117). This stems from combination of following characteristics (1) the parent clays are transparent in the near UV and visible range of the spectrum; (2) they can be expanded or pillared; (3) they can be pillared with compounds that emit radiations (luminesce) or that absorbs radiation (coloured) and (4) they can adsorb other compounds or cations that may influence their property.

Some important luminescent propping molecules are rare earth ions such as, Eu$^{3+}$ and Tb$^{3+}$ etc. and Cr compounds e.g. Tris (2,2' - bpy) Cr(III).

1.4.6 Optical resolution on a clay chelate adduct

Yamagishi (1985) (118) developed a novel method of optical resolution by using a clay-chelate adduct as a chiral adsorbant. It is observed that stereochemical effects on the interactions among the adsorbed molecules on clay is important enough to carry on optical resolution. An optically active metal chelate such as [M (phen)$_3$]$^{2+}$ or [M(bpy)$_3$]$^{2+}$, (where M = Fe, Ru ; phen = 1,10-phenanthroline and bpy = 2,2'- bipyridine) is adsorbed on a clay to form a stereo regular adsorbate layer (119, 120). Racemic mixture Fe(phen)$_3$]$^{2+}$ is adsorbed on the whole surface as racemic pair units, whereas its pure enantiomer is adsorbed only half the cation exchange capacity leaving half of the surface empty (Fig. 1.6)
Fig. 1.6. Schematic presentation of the states of saturated adsorptions of enantiomeric (a) and racemic $[\text{Fe(phen)}_3]^{2+}$ (b)
1.4.7 Metal cluster supported on clay

Metal cluster intercalated clays are unique class of intercalated catalysts (121). In its first investigation (122) Cu⁰ clusters in Mnt act as catalyst in liquefaction of Blind Canyon (Utah) bituminous coal. The Cu⁰ cluster is prepared by refluxing Cu-Mnt in ethylene glycol at 195°C for 6 hrs under Ar. Cu⁰ clusters are 0.4-0.5 nm in size. These catalysts perform with better selectivity in such reactions. In another work Ag-Mnt, hectorite and saponite clays, when irradiated at 77 K, showed formation of Ag₃²⁺ and Ag₄³⁺ clusters in interlayer sites in methanol while no cluster was found in aqueous solvent (123).

1.5 Self-supporting films

Self-supporting films of Mnt are prepared by treating the clay with phosphoric acid (124). Such modified clay exhibits the same CEC and pore distribution as the unmodified clay besides it is stable as film in water even at elevated temperature for prolonged duration. It is assumed that the aluminate edges of Mnt fragments are bridged extensively with each other by the phosphate unit.

1.6 Solid - solid intercalation

Intercalation of organic compounds into Mnt is carried out by solid-liquid or solid-gas reaction. It is found that solid-solid reaction may be applied
to intercalation of compounds not available from solution (125). Solid state formation of smectite-(N-methyl 8-hydroxy quinoline methyl sulphate) intercalation compounds have been reported. (93). The possible role of adsorbed water in case of solid–solid reaction has been suggested in this work. Intercalation is found to occur in case of naphthalene and anthracene into alkylammonium Mnt (126) where the driving force can be explained as hydrophobic interaction between alkylammonium Mnt and the organic compounds. On the other hand, [M(phen)$_3$]$^{2+}$ (where, M = Co, phen = 1,10-phenanthroline) was found to be intercalated into air dried Mnt interlayer while intercalation was not observed with Mnt dried at 300°C (127). Solid–solid reaction resulted in intercalation of a number of alkylammonium ions.

1.7 Aim and objective of the present work

1. Swelling of interlayer cations in Mnt is a complex mechanism. This is to be studied under condition such as different relative humidity and different interlayer cations.

2. Intercalation and intersalation reactions of metal complexes with Mnt has not been studied systematically. Therefore, intersalation of trisdiimine metal complexes are to be studied under different reaction conditions to find the shortest reaction period. Effect of presence of salts on intersalation of the metal complexes is to be evaluated. Moreover, influence of fractionation of the clay on intersalation is also to be considered.
3. Intersalation reaction of trisdiimine metal complexes with Mnt is to be studied for different states of clay i.e. aggregated, dispersed and delaminated. Also, influence of flocculation of Mnt by different concentrations of NaCl on intersalation reaction of the metal complexes with clay is to be studied.

4. Thermal study of clay intercalated metal complexes containing tridentate ligands is to be carried out. The thermal study will be assisted by XRD, IR spectroscopic and elemental analyses.

5. Phosphate linked Mnt and its intercalation / intersalation behaviour is to be studied. Different XRD, IR spectroscopic, thermal and SEM-EDX analyses is to be carried out.

6. Preparation of metal-metal complex-clay composites useful as Friedel-Crafts catalysts is to be carried out. The metal ion used will be Al\(^{3+}\) or Zn\(^{2+}\) while the pillaring species will be large cations like [Ni(phen)\(_3\)]\(^{2+}\).

7. Adsorption of toxic gases like hydrogen sulphide, ammonia and mercaptanes by metal-metal complex-clay composites is to be studied. The metal ions used will be Cu\(^{2+}\) or Cd\(^{2+}\) while the pillaring species will be large cations like [Ni(phen)\(_3\)]\(^{2+}\) or [Ni(bpy)\(_3\)]\(^{2+}\).

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