

CHAPTER - 1

INTRODUCTION AND REVIEW OF PREVIOUS WORK

1.1. The Clay Mineral

The clay minerals are, in general, silicates of either aluminium or magnesium. Two very simple units of structure are common to all : the silicon tetrahedron, modified somewhat as to size when the larger aluminium atom proxies for silicon, and the aluminium octahedron in which the central atom, usually aluminium, magnesium or iron, is surrounded by six oxygen atoms. All the crystalline clay minerals have in common a two dimensional arrangement of silicon and oxygen, forming a hexagonal sheet of composition $\left[(\text{Si}_2\text{O}_3)^{2+} \right]_n$. The oxygens satisfying the fourth silicon valency normally form a second sheet of composition $\left[(\text{O}_2)^{4-} \right]_n$, less closely packed than the first. This second unit seldom appears alone, and its identity is submerged in a layer of fairly close-packed oxygens and hydroxyls contributed to both by the oxygens accounting for the fourth valency of the silicon, and also by hydroxyls in octahedral arrangement around aluminium or a similar atom. The unit $\left[(\text{Si}_2\text{O}_3)^{2+} \right]_n$ takes two forms. In one all the silicon atoms are on the same side of the oxygen sheet. In the other the silicon atoms alternately form strips on either side of it. The first form is found in the kaolin group, the montmorillonite group, the hydrous mica group and the chlorites. The second form constitutes the distinctive unit of the attapulgite-sepiolite-palygorskite group and links them structurally with the hornblendes.

From the X-ray diffraction studies on the mica, talc, pyrophyllite, chlorite and kaolinite, Pauling^{1,2} on the basis of crystal chemical concept had suggested an essential similarity between these materials regarding the dimension of their unit cell in the plane of cleavage and suggested that these materials have a layer-structure composed of sheets of cristobalite, SiO_2 and either gibbsite, $\text{Al}_2(\text{OH})_6$ or brucite $\text{Mg}_3(\text{OH})_6$. The layer of silicates or phyllosilicates are believed to form by condensation of sheets of linked $\text{Si}(\text{O}, \text{OH})_4$ tetrahedron with $\text{M}_{2-3}(\text{OH})_6$ octahedron, where M is either divalent or trivalent cation. According to the type of condensation the clay minerals may be classified in three distinct categories, are designated as 1:1 (or dimorphic), 2:1 (trimorphic) and 2:2 or 2:1:1 (tetramorphic), depending on the ratio of tetrahedral to octahedral sheets in one repetitive layer. Thus, kaolinite belongs to the 1:1 type, montmorillonite and mica to the 2:1 type, and chlorite to the 2:1:1 type, Palygorskite and sepiolite also have a basic 2:1 layer, although this is sharply limited in one direction with inversion of the sheet around an oxygen atom, resulting in a chain like structure with channels along the fiber length.

Isomorphous replacement frequently occurs (e.g. when Al^{3+} is replaced by Mg^{2+}) in some of these minerals leading to a charge on the sheet surface satisfied by cations external to the layer, which may or may not be readily exchangeable with others from solution. The charge density on the sheet surface has important

repercussions, since variation in its magnitude give rise to minerals with different properties - e.g. as regards swelling in water or other polar liquids - and must be considered as a principle in defining groups. The electron charge per layer-unit-cell in the 2:1 type varies from 0 to 4. At a charge of 0, there are no substitutions, no extraneous ions, and no swelling in polar liquids; at a charge of about 0.5 to 1, the cation exchange capacity (c.e.c.) is about 100 meq/100 g, and swelling in water is such that complete separation of layers can occur; at a charge of about 1 to 1.5, the c.e.c. is about 150 meq/100 g, and swelling is limited; at a charge of about 2 and higher there is essentially no c.e.c. (apart from some ions on exposed surfaces) and no swelling.

The chemical stability and physical properties varies according to the particular atoms present in the fused silicate unit of the mineral. The manner in which the silicate units are held together is of greater importance in relation to the physical and chemical properties of the clay minerals. Neutral planar silicate units may be packed together in parallel orientation so that successive layers are held together by vander Waals forces. The latter are often thought as of extremely short range, but whereas for isolated spherical molecules the force falls off inversely as the seventh power of the distance, for continuous sheets the inverse function is of the second power only. Hence crystals of talc and pyrophyllite of considerable thickness exist, exhibiting very ready cleavage parallel to the sheets. Neutral

silicate units may be intercleaved with layers of highly polar molecules tending to hold them together. In the kaolin group, there are layers of OH groups, the hydrogen atoms of which tend to form hydrogen bonds with adjacent layer of oxygen atoms or hydroxyl groups. This hydrogen bonding forms a somewhat stronger junction than that given by vander Waals attraction between layers of oxygen atoms in contact. Nevertheless, layers held together in this way are easily separated by cleavage. As a result of isomorphous substitution by atoms of differing valency in silicate lattice, electrostatic charges arise which must be balanced in the completed crystal. According to Pauling's rule, they must be balanced over the shortest possible distances. In the muscovite micas, the negative charge arising by the substitution of Al for Si in the silica sheets is balanced by K atoms. Geometrically these are accommodated between successive rings of six oxygen atoms in adjacent units and may be regarded as a positively charged electrostatic cement holding the negatively charged sheets together. The strength of such a bond will depend on the strength and number of the individual linkages per unit area. Where the surface density of electrostatic charges is only moderate, the silicate layers readily admit polar molecules. This is the case in the montmorillonite group, where the separation upto large distances and in the vermiculites, where the intercleaved water is not more than two molecular layers in thickness. The strength of the bond between successive layers is then a very sensitive function of the charge distribution, of the geometry of the "cementing" cation in relation

to the silicate surface and of the structure of the polar molecule.

In our present studies kaolinite and montmorillonite are the two clay minerals used for polymerization reactions, these, therefore deserve detailed consideration.

1.1.1. Kaolinite

Dioctahedral species kaolinite and halloysite of the kaolinite group are the example of 1:1 type of minerals. The structure of the kaolinite layer, together with the manner of stacking of successive layers within a crystal are shown in Fig. 1.

Each layer occupies a thickness of nearly to 0.72 nm, a value equal to the basal $[d(001)]$ spacing of kaolinite. As shown in the figure, the kaolinite is electrically neutral but in reality it carries a small negative charge due to a less amount of isomorphous replacement^{3,4}. This 'permanent' - as opposed to the 'pH dependent' - negative charge⁵ is responsible for the small but measurable (0.1 mol kg^{-1} , monovalent cations) exchange capacity of kaolinite samples under acid conditions. Hofmann et al⁶ proposed that the exchange sites are located on only the tetrahedral surface of the kaolinite crystal. The superposition of oxygen and hydroxyl planes of successive layers within a single kaolinite crystal gives rise to pairing of O and OH ions and interlayer $\text{O} \cdots \cdots \text{HO}$ H-bond formation. Clearly the forces arising from H bonding and those due to non-specific vander Waals interactions holding adjacent layers together, must be overcome if interlayer sorption (intercalation) of extraneous species is to occur. For this reason,

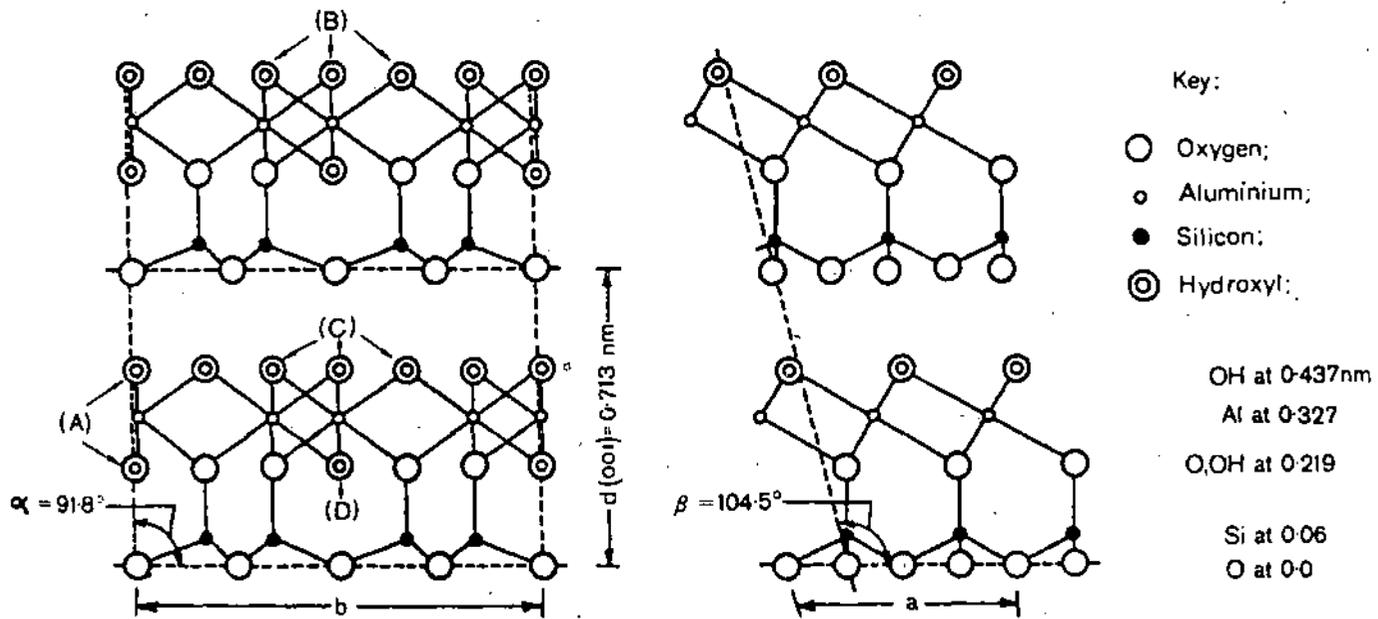


Fig. 1 Kaolinite layer viewed along the *a* axis (left) and along the *b* axis (right). Height of atoms above the basal oxygen plane are given in nanometres (nm), from Brindley

penetration of kaolinite interlayers by organic compounds is difficult to achieve and adsorption is generally confined to the external crystal surfaces. It can now be recognised that the edges of kaolinite crystals are of particular importance. This is because the edges containing unsatisfied valencies ('broken bonds') occupy an appreciable proportion (10-20%) of the total crystal.

1.1.2. Montmorillonite

The structure of montmorillonite was first given by Hofmann, Endell and Wilm⁷ on the basis of its similarity with that of pyrophyllite (Fig. 2). This basic structure into which modifications by Marshall⁸, Maegdefrau and Hofmann⁹ and Hendricks¹⁰ were subsequently incorporated, is now generally accepted^{11,12}. The montmorillonite layer differs from that of pyrophyllite in that substitution of Al^{3+} for other cations (e.g. Mg^{2+} , Fe^{2+}) in octahedral positions and less frequently of Si^{4+} for Al^{3+} in the tetrahedral sheet, always occur. Although some internal compensating substitution may occur, the final result of isomorphous replacement in the pyrophyllite structure is a layer which carries a permanent negative charge. This positive charge deficiency is balanced by sorption of exchangeable cations which, apart from those associated with external crystal surfaces, are situated between the randomly superposed layers within a crystal⁹. Water is also readily adsorbed in the interlayer space. These concepts are illustrated in Fig. 3.

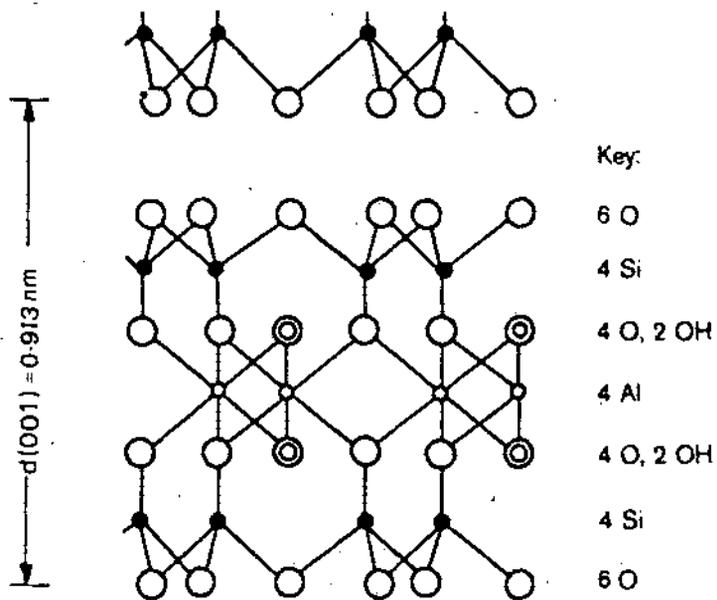


Fig.2. The pyrophyllite layer structure viewed along the a axis. The basal spacing ($d(001)$) is given in nanometers.

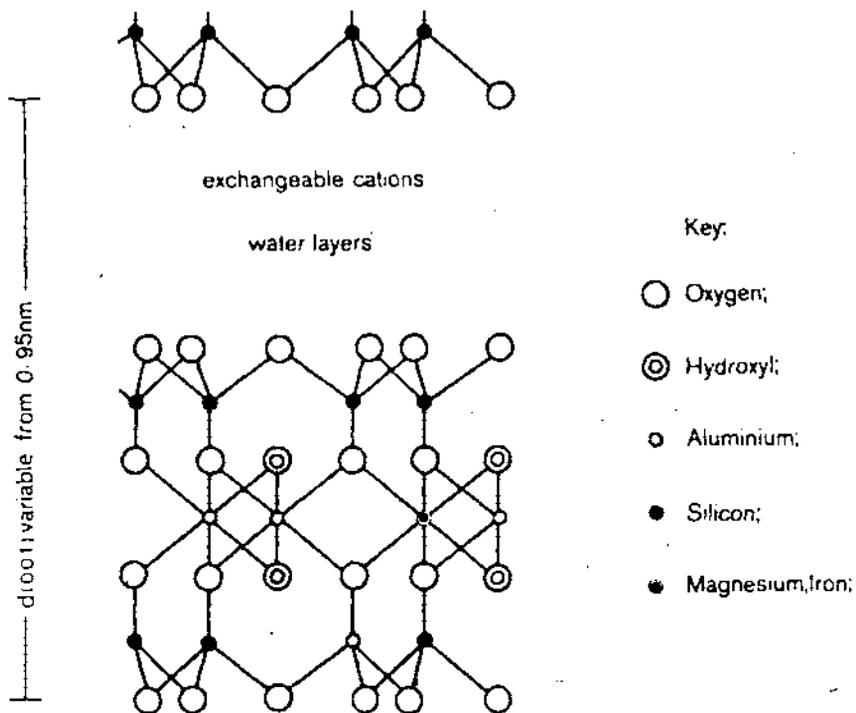
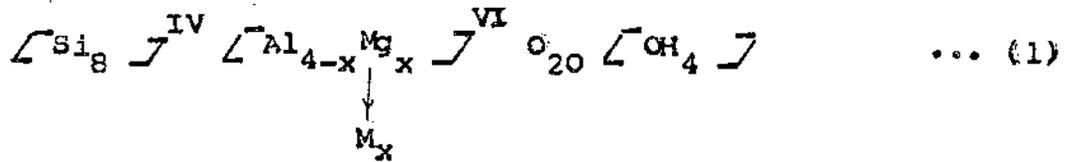


Fig.3. The structure of a montmorillonite layer viewed along the a axis. The basal spacing is given in nanometer units.

Water appears to enter the inter layer region as an integral number of complete layers of molecules, this number being dependent on the nature of the exchangeable cation¹²⁻¹⁴. The d(001) spacing of montmorillonite can thus vary over a wide range, the minimum corresponding to the fully collapsed state being 0.95 nm. With large monovalent and divalent cations occupying interlayer (or inter crystalline) swelling is limited to a d(001) spacing of about 1.9 nm. On the other hand, montmorillonite samples saturated with small, monovalent cations (Li^+ , Na^+) may show extensive inter-layer expansion in dilute aqueous solutions (nearly to 0.3N) of their respective cation salt and in water, and under optimum conditions the layers can dissociate completely¹⁴. The charge density on the clay surface as well as the nature of the exchangeable cation has a profound influence on the hydration properties of 2:1 type phyllosilicates and obviously the hydration properties are affected more by the interlayer cation than by the silicate surface. Since uncharged polar organic molecules are adsorbed essentially by replacement of the interlayer water, the behaviour of such molecules is likewise strongly influenced by the exchangeable cation. Evidence is accumulating to show that, at least at low water contents, cation-dipole interactions are of paramount importance in their effect on the adsorption of polar molecules by clay minerals.

Montmorillonite acquires its charge by the replacement of octahedral Al by Mg atoms. The structural formula is written as



This formula gives the composition of the planar unit cell. The number IV and VI indicate tetrahedral and octahedral positions respectively. The symbol M_x indicates the presence of compensator cations totalling x valencies per cell. The charge x is generally between 0.5 and 0.9. Formula (1) is idealized; Fe^{3+} replaces a part of the Al's, and Fe^{2+} replaces a part of the Mg's. Extensive chemical studies especially on the changes in composition smectites by base exchange and the swelling effects in their geometrical significance, were made by M.D. Foster¹⁵. Swelling decreases with increasing octahedral replacement. In this respect the introduction of Fe^{2+} into the octahedral layers has a greater depressing effect than that of Fe^{3+} which in turn appeared to have the same depressing effect as Mg^{2+} .

An alternative and completely different structure (Fig. 4) for montmorillonite has been suggested by Edelman and Favejee¹⁶. The main aspect of this structure is that every alternative SiO_4 tetrahedron in the tetrahedral sheet is inverted. The apical oxygens of such inverted tetrahedra, now pointing away from the surface, are replaced by hydroxyl groups which also fills the gaps left in the octahedral sheet. No isomorphous replacement within the structure is envisaged and the observed cation exchange capacity being solely ascribed to the dissociation of apical hydroxyl groups.

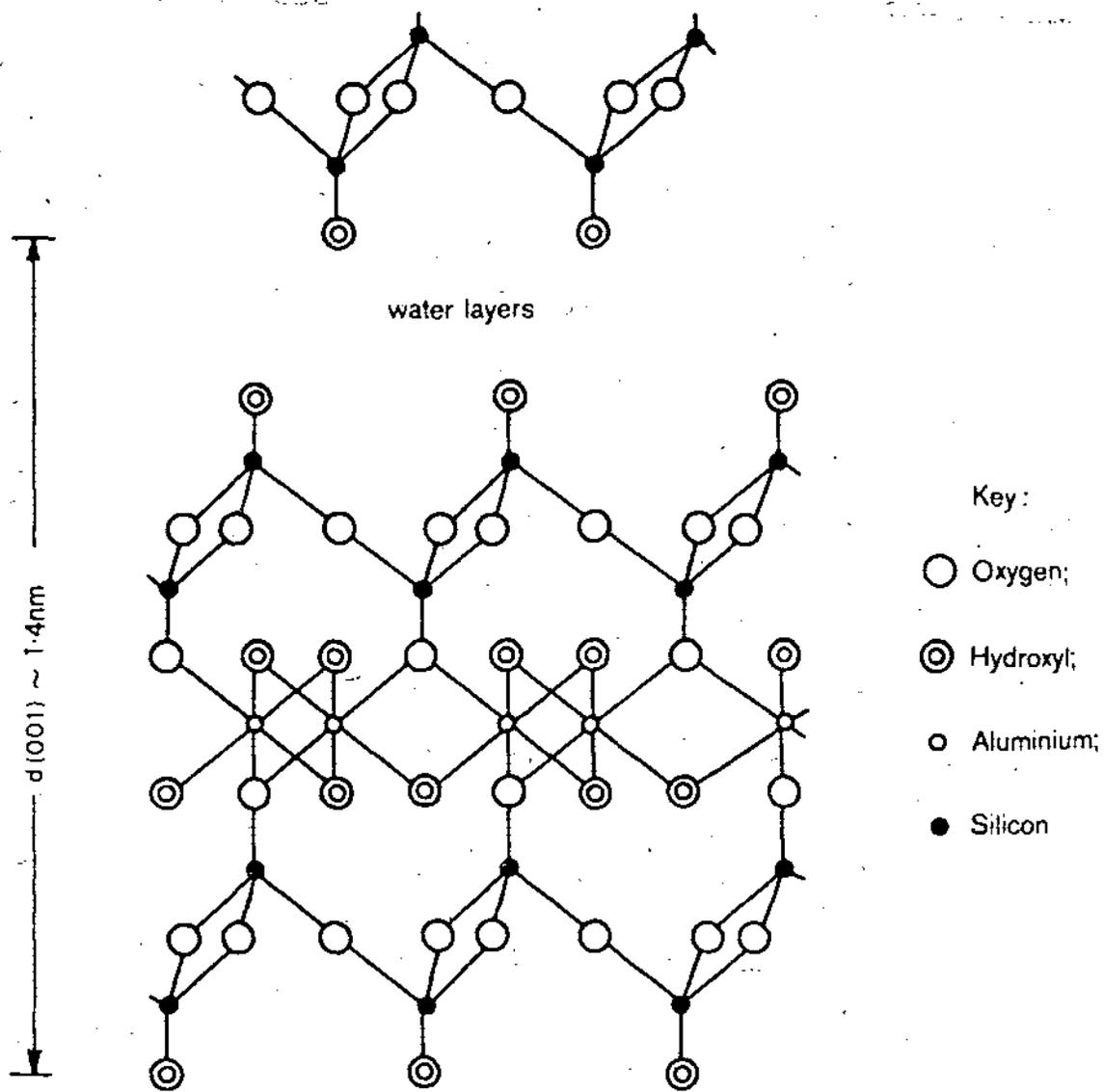


Fig. 4. The montmorillonite layer structure viewed along the a axis according to Edelman and Favejee. Basal spacing in nm units

Somewhat similar structure in which excess hydroxyls are present due to the replacement of some Si^{4+} ions by $4H^+$ or $Al^{3+} H^+$ ions in the tetrahedral sheet has been suggested by McConnell¹⁷. On the other hand, Grim and Kulbicki¹⁸ postulated the existence of two types of montmorillonite, one conforming to the Hofmann-Endell-Wilm-Marshall-Maegdefrau-Hendricks structure and the other to the Edelman-Favejee structure. Because of the poorly crystalline nature of the clay mineral, X-ray diffraction patterns are generally broad and diffuse. Moreover, obtaining homogeneous and uncontaminated samples is not an easy task. These facts make it difficult to discriminate between the various possibilities using X-ray analysis alone. By a combination of X-ray, DTA, TGA and chemical analysis, it has been possible to distinguish between four types of montmorillonite and 'non-ideal' types and between 'ideal' and 'non-ideal' beidellites. The 'ideal' type has 4OH groups per unit layer cell (a unit cell being twice the formula unit).

Studies on the surface esterification of montmorillonite and related silicate minerals by Berger¹⁹ and specially by Deuel²⁰ and co-workers have been explained in terms of the existence of surface silane groups, thus favouring the Edelman-Favejee concept. Apart from restrictions imposed by accessibility and steric factors, these hydroxyl groups are capable of reacting with certain organic compounds (e.g. CH_2N_2 , $SOCl_2$, alkyl chlorosilanes) to yield covalently bonded organic complexes.

In montmorillonite less than 10% and more commonly only 2-3% of the total (external crystal and interlayer) area of nearly to $760 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ is apportioned to the crystal edges. Hence, the influence of the crystal edges on the pH-dependent charge and sorption of anions, electron transfer reactions involving organic compounds, and the initiation and/or inhibition of polymerization of organic monomers is much more in evidence with kaolinite than with montmorillonite and mica-type minerals.

It is very much desirable that the recent analytical techniques to study clay systems and their chemistry should be briefly dealt with - as these are now available to the modern research workers. Though most of these methods have not been exploited in the present study due to non availability of instruments it may be visualised that use of these techniques in near future will throw considerable light on many of the unanswered questions that we face in the domain of clay organic reactions.

Mossbauer Spectroscopy: This is based on the resonance or recoilless absorption of γ -rays emitted by special nuclei during their decay from an excited nuclear state to the ground state. Many nuclei have spins arising from the angular momentum of their proton and neutrons. The spin states are quantized so that a nucleus with a spin 'I' can have (2I+1) energy states and transitions can occur between the ground and excited states, subject to the selection

rule that the change Δml must be \pm or 0. The principal parameter that is obtained from the Mossbauer spectrum is the isomer shift which depends on the 's' electron density and this in turn, depends on the chemical environment of the nucleus. This provides information on the oxidation state and the co-ordination number also. In addition to the isomer shift to the main transition, quadruple splitting of the $3/2$ level arises due to non-uniform charge density. Further splitting of the energy levels takes place in a magnetic field and thus six transitions are possible (Nuclear Zeeman effect) ^{57}Fe is the most important Mossbauer nucleus for investigation of soils and clays. Mossbauer spectroscopy has been used to differentiate the crystallographic positions occupied by Fe^{2+} or Fe^{3+} in pyroxines and amphiboles, which chemical techniques are unable to distinguish. In the 2:1 layer silicate minerals octahedral and tetrahedral co-ordination of Fe^{3+} can be distinguished and using information on chemical shift, Fe^{2+} and Fe^{3+} can be distinguished by non destructive techniques. Mineral alterations due to natural weathering, chemical alterations carried out in the laboratory and thermal changes have also been studied. When oxidation-reduction changes take place in systems containing iron, the sites of such changes can also be distinguished. It has found applications in archeology and is especially suitable in the study of amorphous oxides of iron, which generally are not amenable to study by X-rays.

Neutron Scattering methods: Neutron scattering as a practical aid became possible in the mid 1950s when neutron flux of high intensity needed for such studies could be readily produced in reactors. Neutron diffraction is complementary to X-ray diffraction (XRD) studies in that it can determine hydrogen and deuterium atoms also and can distinguish between elements of similar atomic number. Neutron scattering is very useful in the study of lattice defects and solvent phase interactions. In clays, it is used for structure determination of clays and intercalates. Using this technique Rothbauer²¹ noted that OH bonds were oriented at an angle of about 78° to the C axis in muscovite.

X-ray Photoelectron Spectroscopy (XPS) : Photo electron spectroscopy is based on the photoionisation of inner shell electrons of an atom when irradiated with photons of sufficient energy. Kinetic energy of the ejected photo electrons is measured and the number of photo ejected electrons is plotted as a function of their kinetic energy, yielding a photo electron energy spectrum. XPS is ideally suited for studying the chemistry at mineral interphase, as opposed to other techniques which reveal only properties related to the bulk mineral phase. Petrovic et al²² have used this for study of dissolution of feldspars. Koppelman²³ and his associates have used this for study of reactions at mineral phases. This is a relatively little used technique but has much potential in surface studies.

Nuclear Magnetic Resonance (NMR) Spectroscopy : NMR spectroscopy is based on the nuclear spin of atoms. Proton NMR has been used to study the structure of interlamellar water in layer silicates and in halloysite. It has also been used to study the effect of metal ions in altering the structural configuration of water near clay surfaces. It is generally used as complimentary to other methods. Only specific groups in Belgium and USA have used this technique extensively for clay mineral studies.

Electron Spin Resonance (ESR) Spectroscopy : ESR is being increasingly used for structure determination of the clays using para-magnetic probes such as transition metal ions and is based on the spin of electrons. In the absence of a magnetic field, the electrons are oriented at random. In the presence of a magnetic field, it splits into energy levels and transition from one to another is possible. The surface chemistry of minerals is very much dependent on the nature of the exchange ions. ESR is a powerful means of observing the formation of complexes between exchangeable cations and adsorbed molecules on clay surfaces. The complexes will have ESR parameters different from the ions and can be identified. More recently organic free radicals have been used as spin probe to study configuration of adsorbed organic molecules which are generally diamagnetic.

Photo Acoustic Spectroscopy (PAS) : PAS makes use of the non-radiative or thermal decay of the photon excited state of atoms and molecules. The heat emitted changes the pressure of the gas,

surrounding the absorber, which are picked up on a microphone and amplified. PAS is useful for opaque or translucent systems like clay suspensions. The technique has been used successfully in other biological systems, but has found little application in soil systems, though the potential is high.

1.2. Clay-Organic Interactions

Involvement of clay minerals in affecting organic reactions have now been well established by the contributions of Smith²⁴, Giesecking et al²⁵⁻²⁷, Hendricks²⁸, Jordon²⁹, Bradley³⁰, Mac Ewan³¹, Deuel³² and others. Excellent reviews of up-to-date studies are available in books and journals [Grim³³, Eitel³⁴, Theng³⁵, Mac Ewan³¹, Greenland and Hayes³⁶, Sposito³⁷, Brindley & Brown³⁸, Mortland³⁹ and others]. Extensive studies on interaction of organic compounds with clay systems have also been the subject matter of research of different Indian Scientists. In this context the noteworthy contributions of Mukherji^{40,41}, Chakravarti⁴²⁻⁴⁷, Mukherjee and co-workers^{48,49}. De and co-workers⁵⁰⁻⁵³ deserve special mention.

On the basis of the above it has been abundantly clear that clays interact with many organic compounds to form complexes of varying stabilities and properties. These interactions are of great significance and importance in nature and in industry. The association of clay with other organic matter has a multitude of consequences that are reflected in the physical, chemical and biological

properties of the matrices in which they occur. Organic derivatives especially of montmorillonite have so far been obtained either by (a) ion-exchange reactions or (b) by direct introduction of the Si-C linkage. Adsorption of non-ionic organic molecules of polar character by clay minerals has also been investigated in considerable details. It has been noted that small organic ions are adsorbed only upto the cation exchange capacities of the clay minerals while larger ones may be adsorbed in excess. The sorption of organic molecules takes place on the surface of kaolinite which they penetrate between the unit layers of montmorillonite. The pronounced change in the physical properties of organo-clay complexes, particularly in relation to the development of organophilic characteristics, water proofness, exchange and other surface phenomena has been revealed by the work of Jordon²⁹, Gieseck^{25,27}, Mukherji⁴⁰, Chakravarti^{46,47} and others. In the above studies some attempt has also been made to ascertain the nature of the bond in the clay organic complexes.

The adsorption behaviour of quaternary ammonium compounds of varying chain length on surfaces of montmorillonite, kaolinite, vermiculite, soil colloids and clay mixtures has been critically studied by Chakravarti⁴²⁻⁴⁷. Electrochemical, viscometric, electrophoretic and sedimentation volume studies of pure clay minerals and their mixtures in the presence of quaternary ammonium compounds reveal several points of interest for the identification and separation of component clay minerals from mixtures. The complicated process of interaction of larger ions with clays is accompanied

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by significant variation of exchangers, namely, charge reversal^{42,48,50} as shown by electrophoretic and sedimentation volume measurements. It has also been demonstrated that the behaviour of relatively smaller ions such as tetramethyl ammonium ions is almost identical with that of smaller organic ions in respect of exchange characteristics. There are at least two points of difference between the adsorption of higher alkyl organic ions with other inorganic cations. Although the amount absorbed far exceeds the available number of exchange spots the latter are not fully accessible to the added organic ions. This was shown by the residual exchange capacity of the treated clay. The adsorption of cetyl trimethyl ammonium etc. is not reversible in the same sense as that of the ordinary cations and the adsorption is strong enough to be reversed by Ba^{2+} and H^+ ions at concentrations at which other basic cations are generally replaced. In the formation of the clay organic complexes and for their stability the idea of vander Waals and hydrophobic bonds in addition to coulombic bond has been invoked by the author⁴³⁻⁴⁶.

The pronounced change in the physical properties of organo clay complexes, particularly in relation to the development of organophilic characteristics, waterproofness, exchange and other surface phenomena has also been revealed by the researches of Mukherji⁴⁰ and Chakravarti^{46,47}.

Mortland³⁹ has characterised clay organic complexes on the basis of the processes which lead to their formation. These include cation and anion exchange, covalent, hydrogen and ion-dipole bonding and interaction resulting from vander Waals and entropy effects. In addition, charge transfer process and ligand exchange might also take place, specially in organic compounds and humic substances.

Raman⁵⁴ in his paper of 'Surface Chemistry of Soil Minerals' narrated a short but useful discussion on interaction of clays with Organic and Bio active Molecules. He observes that modern day agriculture is dependent on the use of a large number of agro-chemicals, including pesticides, weedicides, soil conditioners and a host of chemicals that promote or modify the water retention and other physical and chemical characteristics of soil. Soil acts as a source as well as a sink for such agro-chemicals; as a source when such agro-chemicals are applied to the soil to suppress weeds, insects and disease organisms and as a sink when it is returned to the soil as fall out from spray, drift, run off or plant and animal debris. It has recently been established that mineral components play an important role in the complexation, bio-activity, release and other associated properties of these agro chemicals. The most important single factor that govern the activity of such agro-chemicals is their sorption-equilibrium as affected by clay minerals since such processes as chemical degradation, transport, persistence and permanent binding are involved. As illustrative examples of

such kind of interactions the interactions of non-polar and polar pesticides with soil have been discussed. The interactions between organic molecules and bio active compounds and even substances like enzymes with clays saturated with different cations have been summarized by Raman⁵⁵.

While most of these studies are on the interaction between clays and defined organic molecules of known structure, another interesting area of study that has gained importance in the recent past is "Clay Polymer Complexes". Theng⁵⁶ in his well written and interesting book, summarises the development in this area and the immense possibilities of studying interactions of clays with synthetic and naturally occurring polymers. The contributions of Mortland⁵⁷, Boyd and Mortland⁵⁸⁻⁶⁰ in this context is very significant. They also reported⁵⁸ dioxin radical formation and polymerization on Cu(II)-smectite under mild reaction conditions and indicated this as a possible decontamination procedure for hazardous wastes containing dioxins. These and other studies indicate the interesting possibilities of manipulating even biological reactions using clay minerals and their surface chemical properties.

Montmorillonite and vermiculite minerals readily form interlayer complexes with a variety of uncharged polar organic molecules. In addition, these minerals and their complexes with organic materials can yield thin, self supporting films with good infra-red transmission properties. A better understanding of the behaviour of polar organic compounds at the clay surface has come

from examination of their complexes with montmorillonite and to a lesser extent, of those with vermiculite. Till 1960's, X-ray diffractometry was used almost exclusively to study the structure of the complexes formed between expanding 2:1 type layer silicates and organic compounds. While this method has yielded much useful information on the arrangement and conformation of the organic molecule in the interlayer space of such minerals⁶¹⁻⁶³, its usefulness in investigating those changes that may take place in the structure of the adsorbed compound is limited. The establishment of structure and crystallinity of the main groups of layer silicates related to clay minerals initiated studies on the clay organic complexes. It was postulated that complex formation between the clay fraction and the organic constituents of soils is responsible for the stability of the microbial^{64,65}.

The interactions and perturbations occurring at the clay surface of certain structural groups of atoms in the organic molecule often give rise to changes in the position and/or the intensity of the corresponding vibrational bands in the spectrum of the complex, as compared with similar bands in the spectrum of the unadsorbed compound. These observations enable conclusions to be drawn regarding the mode of bonding of the intercalated organic molecule to the mineral surface. Infra-red spectroscopy is thus singularly suited for the study of clay-organic interactions. Its use in conjunction with and complementary to classical X-ray diffractometry has been

instrumental in clarifying many of the mechanisms underlying the formation of complexes between layer silicates and organic substances^{39,66}.

Water is perhaps the most common polar compound present in the interlayer space of montmorillonites and vermiculites. Water is also intimately involved in the binding and transformation of polar organic compounds at the surface of these minerals^{39,66-68}. Walker and co-workers demonstrated the presence of two distinct types interlayer water in vermiculite crystals⁶³ from X-ray diffraction studies. The first type (I) constitutes the inner (primary) hydration shell around the exchangeable cation, that is, the water which is directly coordinated to the cation. The second type forms the outer (secondary) coordination sphere of the cation; being indirectly linked to the cation and possessing greater mobility, this water is more labile than that of type I. It is now well accepted that the size and valency and hence the polarizing power of the exchangeable cation plays a decisive role in water absorption. This has been further supported by the infra-red spectra of water adsorbed on layer silicates⁶⁹⁻⁷². The broadening of the absorption band below 3500 cm^{-1} has been assigned to OH groups associated with the intermolecular hydrogen bonds. The preferential adsorption of polar organic compounds on the clay surface occurs due to the interaction between adsorbate and exchangeable cation. It might thus be expected that the removal of much of water from the clay surface would cause the cation to polarize the residual water molecules in the primary hydration

shell. This results in the dissociation of water molecules and the proton generated are involved in the initiation of colour⁷³, polymerization⁷⁴ and decomposition reactions^{67,75}.

Hofmann and Brindley⁷⁶ reported appreciable adsorption of non ionic aliphatic compounds chain length C₅ to C₁₀ on calcium-montmorillonite. But little or no adsorption of short chain organic compounds on montmorillonite from dilute solution (less than 0.5M) occurred. However, German and Harding⁷⁷ have reported that calcium and sodium montmorillonites adsorbed adequate amounts of primary n-alcohols viz. Ethanol, propanol and butanol. This deviation from chain length rule of Hofmann and Brindley has been supported by Bradley for adsorption of some aliphatic amines⁷⁸. Larger molecules with more than five units - both aliphatic and aromatic - may be adsorbed to an appreciable extent by montmorillonite in the presence of excess water⁷⁶⁻⁸⁰. That is, they can displace the water molecules associated with the exchangeable cations. The increase in affinity with molecular size or chain length can be generally applied to the adsorption of organic compounds by clays⁶¹ and is attributed to the increased contribution of vander Waals forces to the adsorption energy. As the size of the molecule increases, vander Waals interactions become important because these forces are essentially additive and tend to orient the molecule so that the maximum number of contact points is established^{81,82}. The adsorption of one organic molecule is accompanied by the desorption of a number of water molecules initially coordinated to the cation, an appreciable amount of entropy is gained by the system, favouring adsorption. Thus, entropy effects arising from multiple bond

formation between the organic compound and the water molecules in the primary hydration shell contribute to the strong adsorption of some uncharged linear polymers by montmorillonite^{83,84}. Besides chain length (molecular size) the chemical character of the organic molecule influences adsorption behaviour. For many aliphatic compounds, a useful index of character is their "CH activity" arising from the activation of methylene groups by neighbouring electron withdrawing substituents like $>C=O$ and $-C\equiv N$. At equilibrium concentration, the amount of $C_6 - C_7$ organic compounds of different functional groups adsorbed on the clay mineral is in the order :

α -methoxy-acetyl acetone $>$ acetoacetic ethyl ester $>$ β -ethoxy propionitrile hexanedione-2,5 $>$ hexane diol-1,6 $>$ 2,4-hexadiyne-diol-1,6⁷⁶.

Complex formation with polar organic compounds is profoundly affected by the nature of exchangeable cation and by the water content (hydration status) of the clay. Apparently, hydration of the clay facilitated acetone uptake, presumably due to the expansion of mineral interlayers. In an attempt to prepare acetone complex, it was found that dehydrated calcium montmorillonite invariably yielded as double-layer complex whereas the corresponding sodium clay gave either a single or a double layer complex⁸⁵. This difference between calcium and sodium montmorillonite in their behaviour towards polar organic liquids accords with later findings of German and Harding⁷⁷ and Bissada et al⁸⁶ for ethanol-montmorillonite and acetone-montmorillonite systems and is ascribable to the greater solvation energy of the calcium ion compared to that of sodium ion.

The formation of double layer complexes of montmorillonite with some ethers and polyethers and one layer complexes of halloysite with some alcohol-ethers has been reported^{78,85}. From X-ray data the basal spacings of 1.31 - 1.34 and 1.57 - 1.76 nm were suggested for both single and double layer complexes respectively⁷⁶.

A comparative study for the adsorption of aceto-acetic ethyl ester, β, β' -oxydipropionitriles, 2,5-hexanedione and triethylene glycodiacetate from aqueous solutions on gibbsite, kaolinite and montmorillonite showed the expected highest adsorption on montmorillonite due to its largest surface area compared to all other minerals⁸⁷. Gibbsite, on the other hand, showed the highest adsorption when the results are expressed per unit surface area or as an equivalent number of packed organic layers. In the absence of any exchangeable cation in gibbsite, cation-dipole interactions can not be responsible for the uptake of polar organic molecules. As gibbsite is composed of hydroxyl ions, it would seem that O-H-O bonding is important.

The complex formation between aliphatic or aromatic amines and 2:1 type clay minerals has received much attention. The basic information available are (i) the amines can exist in the cationic form like the corresponding alkyl ammonium ions which can replace the inorganic cations occupying exchange sites at the clay surface, (ii) adsorption of some primary n-amines by hydrogen montmorillonite is influenced by the pH of the system and by the size (chain length) of the organic molecule.

In acidic media, amides may accept a proton on either the oxygen or the nitrogen atom. From infra-red studies of acetamide, Tahoun and Mortland⁸⁸ have confirmed that amides predominantly protonate on the oxygen atom in acidic montmorillonite systems. Thus O-protonation decreases the double bond character of the C = O group while that of the C-N group is increased, causing a reduction and an increase in the respective absorption frequency. Further, the acquisition of a positive charge on the nitrogen atom would reduce the NH force constant and concomitantly increase hydrogen bonding interactions leading to a decrease in the NH stretching frequency relative to the neutral molecule. Weismiller⁸⁹ has examined the interlayer expansion of montmorillonite and vermiculite crystals in N-ethyl acetamide. Irrespective of the kind of the interlayer cation present, montmorillonite apparently expands to a basal spacing of about 2.05 nm which is interpreted in terms of the intercalation of three layers of N-ethyl acetamide molecules with the exchangeable cations occupying positions midway between two opposing silicate layers. In the initial stages of adsorption, the amide molecule coordinates to the interlayer cation through the oxygen atom, but as the amount present increases the 'excess' amide may form hydrogen bond to the cation-linked species and/or to the oxygen ion of the silicate surface.

Weil-Malherbe and Weiss⁹⁰ showed that both acid base interactions and oxidation - reduction reactions were involved in the formation of coloured clay complexes with certain aromatic amines. The former mechanism predominates with acid washed clays which can act as proton donors (Bronsted acids) since the activity

of the mineral can largely be suppressed by treatment with a base, such as ammonia. Oxidation-reduction reactions, on the other hand, are relatively insensitive to either acid or base pretreatment of the clay but are markedly influenced by the presence of reducing agents, such as stannous chloride. The operative mechanism here is apparently one of electron transfer from the adsorbed species to the clay acting as an electron acceptor (Lewis acid). Following Briegleb⁹¹ such association between clays and organic compounds may thus be termed electron-donor acceptor complexes. In the colour reactions of clays with aromatic amines both Lewis and Bronsted acidities are involved. Adsorption of the organic molecules is controlled by the electron transfer and by cation exchange processes occurring at both the edge and the basal surfaces of the clay crystals. These observations have led to Solomon et al⁹² to propose a model based on charge transfer between the mineral and the adsorbed organic species. The oxidation of benzidine to benzidine-blue⁹² on silicate minerals is believed to occur at aluminium atoms exposed at crystal edges and at transition metal atoms in the higher valency state present in the silicate lattices. All montmorillonites give a blue colour when treated with aqueous solutions of benzidine but the intensity of the colour varies widely from light to dark blue (blue colour appears due to benzidine radical-cation formation through electron transfer from benzidine to the mineral).

Montmorillonite which give the more intense colour have ferric ion present in the silicate lattice, although other transition metals in the higher valency state would be expected to behave

similarly. Pale blue colours are given by montmorillonites which do not contain significant amounts of iron, or by montmorillonite in which the iron is in the ferrous form. The deep blue colouration results on reaction of benzidine and montmorillonite in the presence of water, the colour changing through green to yellow on drying. Although it is generally agreed that the blue colouration is due to formation of the positively charged radical cation of benzidine, there are conflicting theories concerning the origin of the yellow colour. Direct ⁵⁷Fe Mossbauer spectroscopic evidence has been, however, presented for the involvement of lattice substituted iron (III) as an electron accepting site, within montmorillonite, following intercalation of the clay by benzidine which results in the production of benzidine radical cations. The subsequent oxidation of the resulting Fe(II), by dehydration of the benzidine blue-montmorillonite intercalate, was explained in terms of two simple equilibria which are set up at the clay surfaces. New Lewis acid sites [involving iron (III)], created by oxidation of the original iron (III) ions in the clay, have conditions where it is expected that benzidine species are present only at external surfaces of the montmorillonite. The electron transfer reaction between the clay mineral and adsorbed organic species are very much important on the studies of clay-organic interactions.

1.3. Clay Catalyzed Polymerization

Synthetic and naturally occurring clay minerals are used in a number of widely diversified roles in the chemical industry as catalyst for cracking⁹³ or depolymerization, alkylation⁹⁴, isomerization⁹⁵, polymerization⁹⁶ etc. The role of clay minerals in influencing the polymerization of organic monomers has been recognized for many years. The behaviour of the clay minerals to initiate the polymerization is similar to that of the common chemical initiators. In addition, the mineral can also inhibit the propagation and/or formation of reactive intermediate species for polymerization. Prior to 1960 dry clay and non-polar solvents were employed for vinyl polymerization as the activity of the dry clay was believed to be augmented in non-polar reaction media⁹⁷⁻⁹⁹. Butadiene, trans- and cis-butene-2 was found to be spontaneously polymerized on the external surface of neutral and acidic montmorillonite at room temperature and atmospheric pressure without additional catalysts⁹⁷. The olefins were adsorbed on dry clay from systems like (i) solid-gas at reduced pressure and various temperatures (ii) solid-gas at room temperature and equilibrium pressure and (iii) solid-liquid at -78° or 0° C for neat monomer or monomer dissolved in solvent.

Although the carbocationic polymerizations of vinyl monomers have been investigated extensively with Lewis acid such as $AlCl_3$, $TiCl_4$, BF_3 , $BF_3 \cdot Et_2O$, BCl_3 alkyl aluminiums etc.¹⁰⁰⁻¹⁰⁶, the first

report on such polymerizations of styrene with acid clays (an aluminosilicate with Lewis acid sites) came in 1964⁹⁸. Almost 100% yield of polystyrene of molecular weights 500 to 2000 was achieved. The catalytic activity of the clay has been shown to be due to active protons associated with tetrahedral (due to dehydration of the mineral) aluminium^{107,108}. The formation of carbonium ion following surface adsorption of olefins on acid sites caused subsequent polymerization. Proton accepting contaminants such as water, amines etc., being preferentially adsorbed over styrene suppressed the polymerization. Styrene polymerized on the surface of the homoionic clays¹⁰⁹. From the comparison of the mineral structure and catalytic activity, it has been shown that dry kaolinite $\left[\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \right]$, attapulgite $\left[(\text{Si}_{3.9}\text{Al}_{0.1}) (\text{Al}_{0.68}\text{FeMg}_{1.22})\text{O}_{1.05} \right]$ were more active than montmorillonite. $\left[(\text{Al}_{2-x}\text{Mg}_x)\text{Si}_4\text{O}_{10}(\text{OH})_2 \right]$ or pyrophyllite $\left[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \right]$. Talc $\left[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \right]$ failed to initiate the polymerization. On the other hand, montmorillonite (2:1 type structure), in spite of coating the edges with sodium hexametaphosphate, yielded traces of polystyrene; whereas kaolinite (1:1 type structure), under similar conditions failed to do so. The polymerization reaction characterizes a free radical as well as an ionic mechanism. It is, therefore, thought that an electron transfer from adsorbed styrene to the aluminium produced radical cations which rapidly dimerized. Both radical cations and dimers are involved in the initiation step but the propagation being cationic. Using activated clay

minerals, however, styrene did not polymerize in the presence of ethanol, dioxane, ethyl acetate and MMA within 30 minutes of the reaction. All these data lead to postulate that the active sites are the octahedral aluminium at the crystal edges. The aluminium acts as electron acceptors.

Matsumoto, Sakai and Arihara¹¹⁰ preferred the concept of Bronsted acidity rather than Lewis acidity to be responsible for the initiation of the polymerization of styrene by montmorillonite. The inconsistency in their experiments, however, is in the reduction of polymer yield in the presence of Trityl chloride which selectively adsorbs on Lewis acid sites. They argued in favour of the Bronsted acidity on the ground that the replacement of exchangeable hydrogen ions by sodium or ammonium ions almost completely inhibited the polymerization. On reacidifying the mineral, however, the activity to polymerize styrene was restored. Since the degree of polymerization increased with the dielectric constant of the medium and was almost independent of the initial concentration, cationic mechanism for the initiation process was favoured¹¹¹. This would apply equally well to the propagation process and, therefore, the initiation by a radical ion mechanism can not be ruled out¹⁰⁹. The possibility of proton transfer to monomer leading to decreased average degree of polymerization, as in conventional cationic mechanism, has also been discussed¹⁰⁷. The contributions of Matsumoto et al¹¹⁰ and Solomon and Rosser¹⁰⁹ lead one to the conclusion that acidity of

the clay can not be solely ascribed to either Bronsted acidity or Lewis acidity. It is to be understood that dry mineral surface is very acidic due to the polarization of residual water molecules by the exchangeable cations. Such acidity is influenced by the solvent as evident from the blue colouration of aqueous benzidine in the presence of oxidized montmorillonite. Instead, a yellow colour appeared when a benzene solution of benzidine was treated with dry clay mineral^{109,112}. Solomon and Rosser failed to find evidence of styrene interacting with the clay mineral which led them to assume that styrene is either incapable of moving into the interlayer space or capable of doing so with difficulty.

The polymerization of MMA on the aforesaid clay minerals did not receive much attention. The failure of MMA to polymerize can be accounted for in the light of well accepted mechanism of charge transfer from the monomer to the clay mineral to produce a radical cation which is a non propagating species for the polymerization of MMA. However, Dekking could prepare MMA-Montmorillonite complex using the conventional free radical initiator, 2-2' azo bis isobutyramidine AIBA¹¹⁹. The polymerization of MMA and methyl acrylate in montmorillonite interlayer induced by γ -radiation has been studied by Blumstein and co-workers¹¹³⁻¹¹⁶. The interlayer polymers were difficult to isolate by the usual solvent extraction and could only be isolated by treating the clay-polymer complex¹¹⁷ with hydrofluoric acid which damaged most polymers. Glavati et al found that polymerization of acrylonitrile/montmorillonite complex

by γ -radiation produced stereospecific polymers.

Thermal polymerization of a number of vinyl monomers e.g., MMA, acrylamide, vinyl acetate, 4-vinyl pyridine could be induced by montmorillonite if AIBA was previously introduced to the clay mineral¹¹⁸. The cationic form of AIBA goes to the exchange sites in kaolinite and montmorillonite to form AIBA-clay complex which decomposes thermally to generate free radicals. The complex has high initiating efficiency. The rate of polymerization with the AIBA-montmorillonite complex initiator was greater than for AIBA alone¹¹⁹. It has been proposed that the free radicals remain attached to the adjacent planes of AIBA-montmorillonite dispersed in water, and on heating, these planes move away from each other allowing more water to penetrate. This situation is graphically represented in Figs. 5 and 6. From X-ray studies it was concluded that type 'c' and 'd' radicals do not recombine but move apart due to driving force of water. Once the radicals are separated some 30\AA , they can initiate the polymerization of the three types of free radicals formed during the decomposition of the AIBA-Clay complex, only type 'a' (Fig. 6) can form homopolymer, and type 'a' radicals are free to be deactivated through recombination with type 'b'. Fig. 6 also explains how the formation of homopolymer may be greatly decreased while the formation of graft polymer (from clay) is increased by decomposing the AIBA-montmorillonite complex. If the clay is dispersed in methanol, the latter surrounds the intercalated free radicals inhibiting their separation and thus facilitating the graft polymer formation.

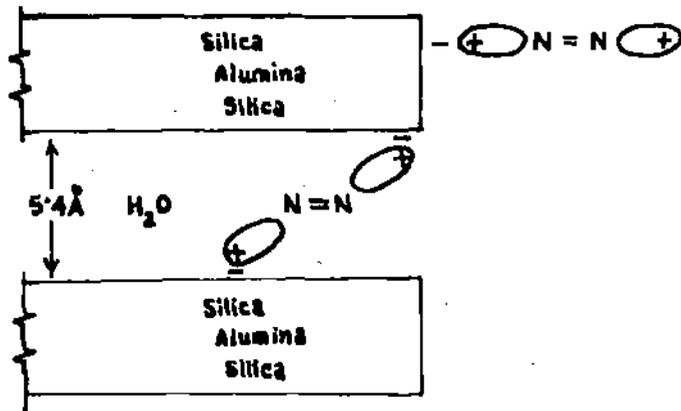


Fig. 5.

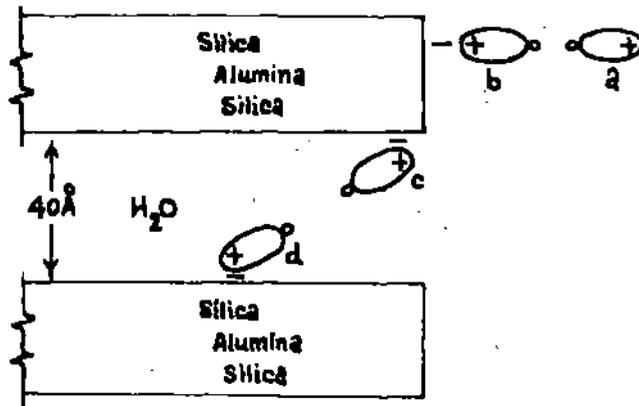
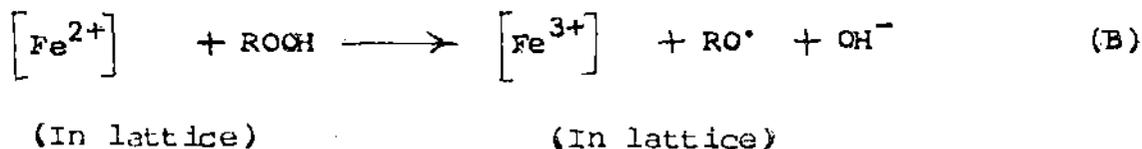
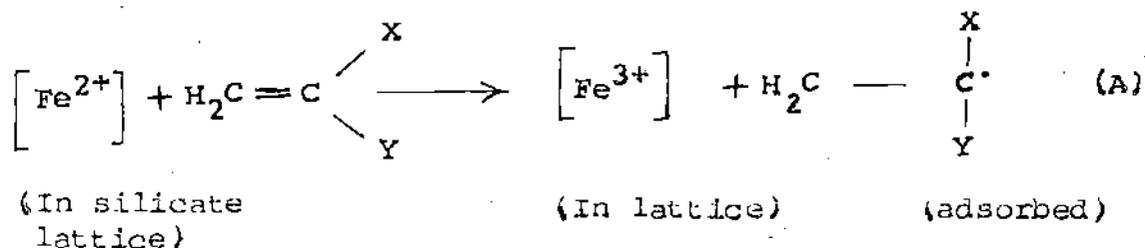


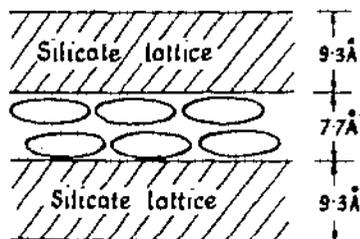
Fig. 6.

From X-ray studies, Solomon and Loft suggested an inter-lamellar complex formation between a series of acrylate and methacrylate monomers and montmorillonite, illustrated by Fig. 7.

Only type III is responsible for spontaneous polymerization of acrylic monomers in presence of peroxide initiator¹²⁰. The polymerization of hydroxy methacrylates has been suggested to be due to the presence of electron donating sites within the silicate lamellae. The inclined orientation of the hydroxyl groups gave a favourable orientation for initiator, and the propagation involved radical anions. The following mechanisms have been forwarded:



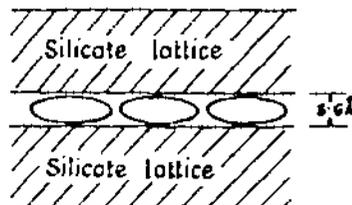
Iron is shown as the oxidizable atom in the silicate lattice although other transition metals may be present. In mechanism (A) the radical anion is formed via electron transfer from the mineral to the double bond. The mechanism is similar to that proposed for the polymerization of olefins by transition metal catalysts.



TYPE I

Two monomer layers lying flat.

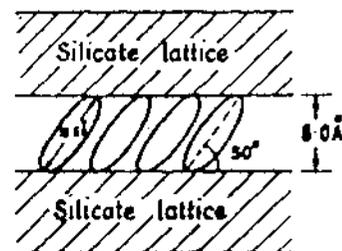
(Spacing shown is for methyl methacrylate)



TYPE II

One monomer layer lying flat.

(Spacing shown is for dimethylaminoethyl methacrylate)



TYPE III

One layer of inclined molecules.

(Spacing shown is for hydroxyethyl methacrylate)

FIGURE 7.

The influence of aluminosilicates and magnesium silicates on the free radical polymerization of MMA has been studied in terms of termination reaction and supported by studies of the reaction of stable free radicals with the minerals. It has been shown that the ability of a mineral to inhibit polymerization follows the order : attapulgite > Kaolinite > montmorillonite > talc. In the absence of clay mineral the yield of polymethyl methacrylate PMMA was 3.68% (mol. wt. 1.36×10^6) whereas with kaolinite and montmorillonite the yields were 0.51% (mol. wt. 2.81×10^6) and 0.68% (mol. wt. 3.05×10^6) respectively. That the decreased amount of polymer in the presence of the mineral is not due to the depolymerization has been established by heating PMMA with kaolinite and determining the viscosity average molecular weight before and after the treatment.

A recent study¹²⁵ on the polymerization of vinyl monomers on clay surfaces shows that MMA, vinyl chloride, and acrylonitrile were homopolymerized and copolymerized with 2-dimethyl aminoethyl methacrylate in the presence of halloysite. The polymer yield can be increased by preheating the mineral with 50% sulphuric acid. The polymerization rate dropped for solution polymerization and among different solvents used the highest polymerization rate was obtained with benzene in the presence of benzoyl peroxide. In redox polymerization in the presence of N-N dimethyl aniline and benzoyl peroxide, the adherence of the polymer to the clay surface was noticed for

both homopolymer and copolymer formed. Among the monomers tested acrylonitrile gave the lowest yield and among the clay minerals, talc was found to be more active for polymerization to occur. However, bonding between the mineral and polymer is least with talc. A recent work¹²⁸ involved ESR study to assess the state of iron in montmorillonites. The absorption bands in the weak field as 'g' values 7.6, 4.2 and 3.9 were assigned to Fe^{3+} ions in the octahedral layer of montmorillonite. The intensities of the wide bands of the spectra remain unchanged when the cations were altered at the exchanging sites. This indicated that the montmorillonite had particularly no iron in the ion exchangeable positions. When the clay mineral was treated with sulphuric acid there was a decrease of the amplitude of the bands for structural iron. The decreased intensities of the narrow bands in the weak field (g = 3.9-7.6) with an increase in sulfuric acid concentration provided a measure of the breakdown of the clay mineral during acid activation.

Studies on the structural properties of the polymers from clay catalyzed polymerizations of vinyl monomers have been made by several workers. Blumstein and co-workers¹¹³⁻¹¹⁶, noted that the thermal stability and dilute solution properties of the polymers prepared in the presence of clay minerals differed significantly from those obtained using conventional free radical technique and suggested that the interlayer PMMA developed a two-dimensional sheet structure in the presence of a cross linking agent during the polymerization. Analysing the n.m.r. data they concluded that

PMMA probably, consisted predominantly of short isotactic sequences. Small scale stereo-regularity of this kind could be ascribed to the orientation induced in the intercalated monomer by ion-dipole and the ester carbonyl group of the monomer. Earlier, Glavati et al¹¹⁷ reported to obtain oriented stereoregular poly(acrylonitrile) and poly(acrylic acid) using similar procedures.

Theng^{126,127} reported that the influence of clay minerals on the polymerization reactions extends beyond direct action on the monomers. The chemical compounds used as polymerization initiators may also be modified by the minerals. It has been observed that clay minerals could affect both the rate and products of decomposition of initiators.

Uskov et al¹²⁸ reported that PVC or a vinyl acetate-vinyl chloride copolymer modified by a latex of Butyl acrylate-methyl-methacrylate copolymer, Butadiene-styrene copolymer, poly(methyl-methacrylate) or a similar polymer was prepared by adding the latex to the reactor during the suspension polymerization. The addition was made after 30-95% conversion of monomers. If inorganic compounds such as silica, montmorillonite, or calcium phosphate was added before or during the polymerization, the polymers with satisfactory particle size separated out from the aqueous suspension.

Recently, it has been reported that bentonite in conjunction with alcohols or thiols^{129,130} effectively initiate the aqueous polymerization of vinyl monomer on the surface of the mineral. A granular soil amendment is formulated from acrylamide polymers,

silicic acid or silicates and one or more of phosphates, nitrates and sulfates, or free from of urea, guanidine, dicyanidiamide, and amidinothiourea¹³¹. The product markedly improves aggregation of clay containing soils. T. Ono. and co-workers¹³², however, polymerized MMA in H₂O containing phyllosilicates such as montmorillonite, talc, and mica in presence of water and azo- initiators. Powder minerals encapsulated with PMMA were formed. When the montmorillonite-encapsulated minerals were extracted with hot benzene or methyl acetate a fraction remained unextractable. The PMMA encapsulated mineral composites had good processability and charpy impact strength. The polymerization of formaldehyde with o- and p-cresol in the presence of Na-montmorillonite results in the formation of linear, short copolymer chains (oriented parallel to the silicate group) in the interlamellar spaces of Na-montmorillonite¹³³. The polymerization of HCHO with m-cresol, did not result in copolymer formation in interlamellar spaces i.e., the high reactivity of the m-cresol resulted in the formation of 3-dimensional copolymers.

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