CHAPTER - I

Section IA : Historical : The clay mineral

Clay minerals are, in general, silicates of either magnesium or aluminium. Oxygens are arranged tetrahedrally around silicon atoms and octahedrally around aluminium atoms; the silicon layers and the aluminium layers are linked through some oxygen atoms of either layer. X-ray diffractions of mica, talc, pyrophyllite , chlorite and kaolinite[1,2] Pauling 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, $Al_2(OH)_6$ or brucite $Mg_3(OH)_6$. The layer of silicates or phyllosilicates are believed to form by condensation of sheets of linked $Si(O,OH)_4$ tetrahedra with $M_{2-3}(OH)_6$ octahedra, where M is either a divalent or trivalent cation. According to the type of condensation the clay minerals may be classified in three distinct categories:

(i) 1:1 type or dimorphic minerals with a general layer formula $M_{2-3}Si_2O_5(OH)_4$. The species are : Kaolinite, Halloysite etc.

(ii) 2:1 type of trimorphic minerals where the octahedral sheet is sandwiched between two sheets of inward pointing tetrahedra (the mica type layer structure). The species are: monmorillonite or bentonite, talc, mica, etc.

(iii) 2:1:1 type or tetramorphic minerals. The species are : Chlorite, etc.

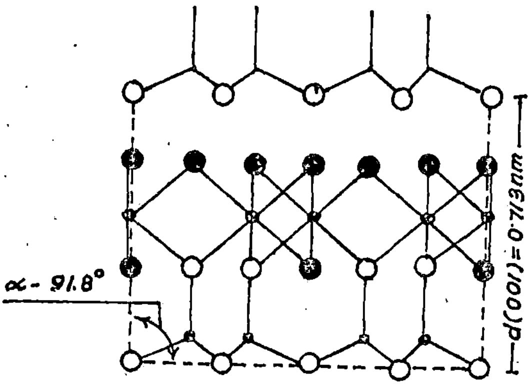
We restrict our choice of clay minerals only to those used for polymerization reaction. Due to unsymmetric cleavage of the sheet of clay minerals charges may grow in them and the charges are neutralised by the absorption of opposite ions that are abundant in the local soil[3]. The kaolinite clay with zero charge per formula unit falls in the 1:1 type of the above classification. With 2:1 type of clay mineral the charge per formula unit is found to be zero for pyrophylite and talc and the charge 0.25 to 0.6 are found for montmorillonite and saponite of different origins. The clay minerals vermiculite and chlorite have the basic unit structure of 2:1:1 type. While the former has 0.6-0.9 charge per formula unit, the later has much varied charge. Depending upon the abundance of the cations in the soil, the exchange of one by another could change the physical properties of the clay minerals. There is scope, in these structures, for isomorphous replacement, i.e. for substitution of Si^{+4} and/or $M^{+2/+3}$ for cations of similar size but different (usually lower) valency. Thus if 3 Mg^{+2} ions replace 2 Al^{+3} ions in the octahedral sheet of pyrophyllite, the mineral is talc. Structural varieties or polymerphism are found in many of the groups (i.e. among any of the variety, say 2:1) because the crystals are composed of discrete layers which can be stacked in a number of different ways.

Interstratification of two or more types of layers within a single crystal is also possible.

A few clay minerals among the three classes, used so far in the polymerization reactions need individual attention.

Kaolinite

Dioctahedral species kaolinite and halloysite of the kaolinite group are the examples 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 below:



○ Oxygen

∘ Aluminium

• Silicon

● Hydroxyl

Fig. 1 Kaolinite layer viewed along a axis

Each layer occupies a thickness of ~ 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 small amount of isomorphous replacement[4]. This 'permanent' - as opposed to the 'pH dependent' negative charge is responsible for the small but measurable (< 0.1 mole kg^{-1}, monovalent cation) exchange capacity of kaolinite sample in acidic condition. Hoffmann[5] et al proposed that the exchange sites of kaolinite are situated only on the tetrahedral surface.

The superposition of oxygen and hydroxyl planes of successive layers within a single kaolinite crystal facilitates pairing of O and OH ions and inter layer O...HO hydrogen bond formation. In other words, the forces arising from H bonding and those due to vander Waals' interactions holding adjacent layers together, must be overcome if interlayer sorption (intercalation) of extraneous species is to occur. 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.

Bentonite/Montmorillonite.

This is a 2:1 type condensate.

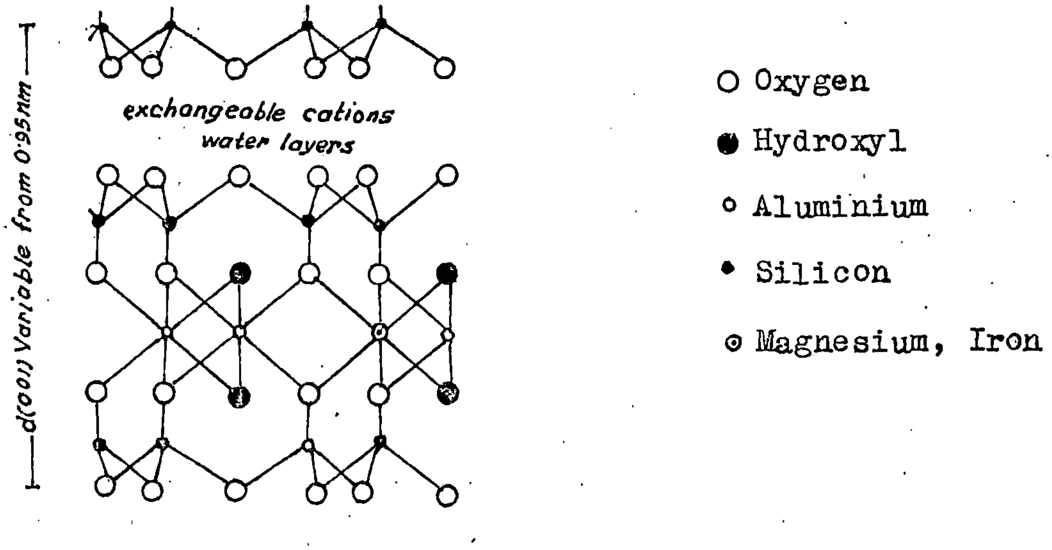


Fig. 2 The Hoffmann-Endell-Wilm-Marshall-Maegdefrau-Hendricks structure of a montmorillonite layer viewed along the axis. Basal spacing is given in nm units.

The structure of montmorillonite was first given by Hoffmann, Endell and Wilm[6] on the basis of its similarity with that of pyrophyllite. This basic structure into which modification by Marshall, Maegdefrau and Hoffmann[7] and Hendricks[8] were subsequently incorporated, is now generally accepted. The montmorillonite layer differs from that of pyrophyllite in that the substitution of Al^{+3} for other cations (e.g. Mg^{+2}, Fe^{+2}) in octahedral positions, and less frequently of Si^{+4} and Al^{+3} in the tetrahedral sheet always occurs. Although some internal compensating substitution may occur the final result of the isomorphous replacement in the pyrophyllite structure is a layer which carries a permanent negative charge[7]. The 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 crystal. Water is also readily adsorbed in the interlayer space[9,10]. These concepts are illustrated in figure 2. Water appears to enter the interlayer region as an integral number of complete layers of molecules. This number depends on the nature of the exchangeable cation. 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 exchangeable sites, interlayer (or intracrystalline) 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 interlayer expansion in dilute aqueous solutions (< 0.3 N) of their respective cation salt and in water, and under optimum conditions the layers can dissociate completely. 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 in consequence 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.

An alternative and completely different structure (Fig. 3) for montmorillonite has been suggested by Edelman and Favejee[11]. The main aspect of the present structure is that every alternate SiO_4 tetrahedron in the tetrahedral sheet is inverted. The apicel oxygens of such inverted tetrahedra, now pointing away from the surface, are replaced by hydroxyl groups which also fill 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. 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 McConnell[12].

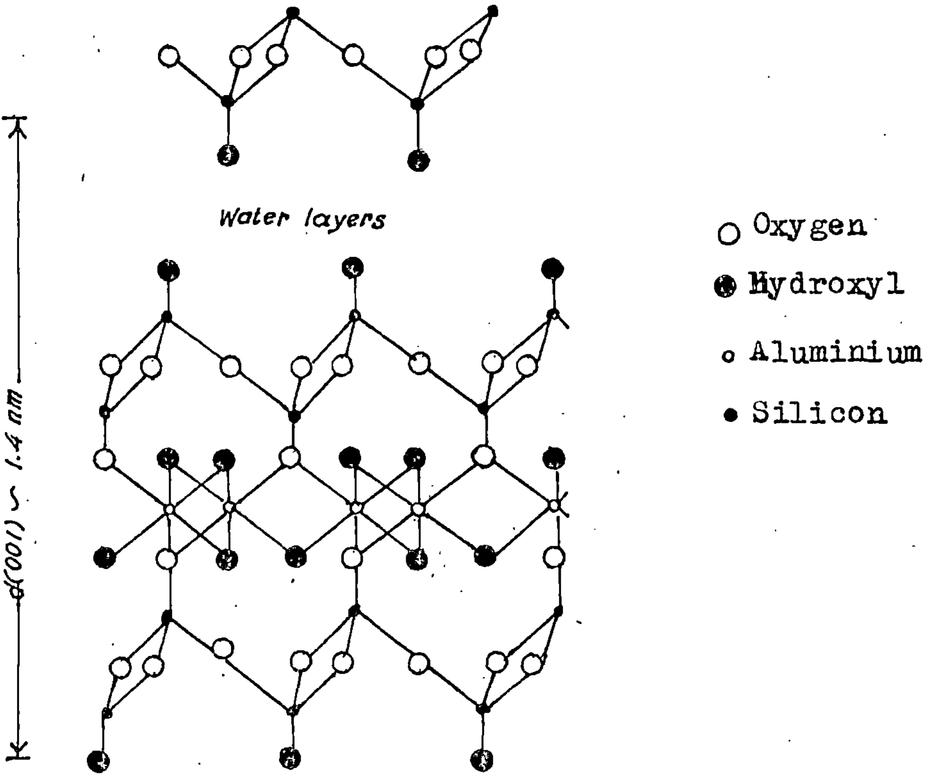


Fig. 3 The montmorillonite layer structure viewed along the axis according to Edelman and Favejee.

On the other hand, Grim and Kulbicki[13] postulated the existence of two types of montmorillonite, one confirming to the Hofmann-Endell-Wilm-Marshall-Maegdefrau-Hendricks structure and the other to the Delman-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 Berger[14] and specially by Deuel[15] and co-workers have been explained in terms of the existence of surface silanol 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 inter layer) area of $\sim 760 \times 10^3$ m^2kg^{-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.

The inter layer expansion and collapse of vermiculite are influenced by the nature of the exchangeable cation as well as by that of the inter layer liquid. In this respect and in its ability to form inter layer complexes with organic compounds,[16] vermiculite bears a striking resemblance to montmorillonite. Any subtle difference between vermiculite and montmorillonite, such as their respective response to contact with organic liquids, are usually ascribable to differences in the amount and location of isomorphous replacement. Thus, Mg -saturated vermiculites fail to expand beyond a basal spacing of ~ 1.45 nm with glycerol (single-layer complex) where as Mg^{+2} -montmorillonite appears to give a double-layer complex with glycerol [$d(001) \sim 1.78$ nm)]. By the same token, the replacement of inter layer inorganic cations by alkylammonium ions in montmorillonite is complete in presence of appreciable amount of aqueous alkylammonium chloride in two hours at room temperature where as much longer period of contact and elevated temperatures are usually required to effect similar exchange in vermiculite crystals.

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SECTION IB

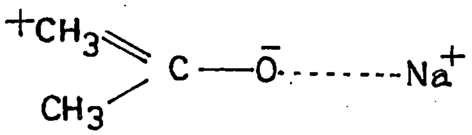
CLAY-ORGANIC INTERACTIONS

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[1-2]. Till 1960's X-ray diffraction was used almost exclusively to study the structure of the complexes formed between expanding 2:1 type layer silicate and organic compounds. The development of infrared spectroscopy along with improved methods of sample preparation has provided means to study the nature of the clay organic bond[3].

Water is perhaps the most common polar compound present in the interlayer space of bentonites and vermiculites. It is now established that water is also intimately involved in the binding and exchange of polar organic compounds on the surface of the mineral[4-6]. Walker and co-workers demonstrated, from X-ray diffraction studies, the existence of two distinct types of interlayer water in vermiculite crystals[7]. The first type (I) constitutes the inner (or primary) hydration shell around the exchangeable cation, i.e., the water is directly co-ordimated to the cation. The second type (II) being the outer (or secondary) co-ordination sphere of the cation where water is indirectly linked to the cation possessing greater mobility. 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 infrared spectra of water adsorbed on layer silicates[8-11]. The broadening of the absorption band below 3500 cm^{-1} has been assigned to OH groups associated with the inter molecular 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 protons generated are involved in the initiation of Color[12], polymerization[13] and decomposition reactions[14,15].

Hoffmann and Brindley[16] reported appreciable adsorption of non ionic aliphatic compounds of chain length C_5 to C_{10} on calcium-bentonite. But little or no adsorption of short chain organic compounds on bentonite from dilute solution (< 0.5 M) occurred. However, German and Harding[17] have reported that calcium and sodium bentonites adsorbed adequate amounts of primary n-alcohols viz. ethanol, propanol and butanol. This deviation from chain length rule of Hoffman and Brindley has been supported by Bradley for adsorption of some aliphatic amines[18]. The complex formation between clay minerals and organic compounds (other than alcohols) of lower boiling points than water is limited due to the evaporation of both the solute and the solvent. In addition, the adsorption on clay surface is greatly influenced by the chemical character of the organic molecules. 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 (m moles) the amount (m mole gm^{-1}) of $C_6 - C_7$ organic compounds of different functional groups adsorbed on the clay mineral in the order : α-methoxy-acetylacetone $>$ acetoacetic ethyl ester $>$ β-ethoxy propionitrile $>$ hexanedione-2,5 $>$ hexane diol-1,6 $>$ 2,4-hexadiyne-diol-1,6[16].

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 bentonite invariably yielded a double-layer complex whereas the corresponding sodium clay gave either a single or a double layer complex[19]. This difference between calcium and sodium bentonites in their behaviour towards polar organic liquids accords with later findings of German and Harding[17] and Bissada et al[20] for ethanol-bentonite and acetone -bentonite systems and is ascribable to the greater solvation energy of the calcium ion compared to that of sodium ion. The IR spectrospopic observation for the adsorption of acetone on sodium bentonite suggests an electrostatic interaction with sodium ion probably through the formation of the following resonance structure[21]



Similar observation has been reported for the complex formation between a number of aldehydes and clay minerals like halloysite and bentonite[19,22].

The formation of double layer complexes of bentonite with some ethers and polyethers and one-layer complexes of halloysite with some alcohol ethers has been reported[18,19]. 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 respectively[16].

A comparative study for the adsorption of acetoacetic ethyl ester, $\beta:\beta'$-oxydipropionitrile, 2,5-hexanedione and triethylene glycoldiacetate from aqueous solutions on gibbsite, kaolinite and bentonite showed the expected highest adsorption on bentonite due to its largest surface area compared to all other minerals[23]. 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 cannot 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.

Apart from alcohols, 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 alkylammonium ions which can replace the inorganic cations occupying exchange sites at the clay surface, (ii) adsorption of some primary n-amines by hydrogen bentonite is influenced by the pH of the system and by the size (chain length) of the organic molecule.

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SECTION IC

CLAY CATALYZED POLYMERIZATION

Clay minerals, due to their favourable structures, have found extensive use as fillers; catalysts for cracking, polymerization etc. In 1960's and earlier clay initiated polymerixations of vinyl monomers emphaized on the use of dry clay minerals and non polar solvents[1-3]. The choice of such reaction conditions was based on the observation that the activity of the dry clay minerals increased in non polar reaction media. Butadiene, trans and cis-butene-2 spontaneously polymerized on the external surface of neutral and acidic bentonites at room temperature and atmospheric pressure without additional catalysts[1]. The olefins were adsorbed on dry clay from systems like (i) solid-gas at reduced pressure at various temperatures (ii) solid-gas at room temperature and equilibrium pressure and (iii) solid-liquid at -78 or 0^oC for neat monomer or monomer dissolved in solvent.

Although the carbocationic polymerizations of vinyl monomers have been investigated extensively with Lewis acids such as BF_3, $BF_3.Et_2O$, BCl_3, $AlCl_3$, $TiCl_4$, $SnCl_4$, alkyl aluminiums etc[4-10], the first report on such polymerizations of styrene with acid clays (an alumino silicate with Lewis acid sites) came in 1964[11]. 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[12,13]. The formation of carbenium 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 also on the surface of homoionic clays[14]. From the comparison of mineral structure and catalytic activity, it has been shown that dry kaolinite $[Al_4Si_4O_{10}(OH)_8]$ and attapulgite $[(Si_{3.9}Al_{0.1})(Al_{0.68}FeMg_{1.22})O_{1.05}]$ were more active than bentonite $[Al_{2-x}Mg_x)Si_4O_{10}(OH)_2]$ or pyrophyllite $[Al_2Si_4O_{10}(OH)_2]$. Talc $[Mg_3Si_4O_{10}(OH)_2]$ failed to initiate the polymerization. On the other hand, bentonite (2:1 type structure), inspite 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,

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* Such nomenclature has been put forward by J.P.Kennedy in "Cationic Polymerization of Olefins: A Critical Inventory", Wiley Interscience, New York, 1975.

ethylacetate and MMA within 30 minutes of the reaction. All these data lead to postulate that the active sites are the octahedral aluminiums at the crystal edges. These aluminiums act as electron acceptors.

Matsumoto, Sakai and Arihara[15] preferred the concept of Bronsted acidity rather than Lewis acidity responsible for the initiation of the polymerization of styrene on bentonite. 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 due to the fact 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 almost independent of the initial monomer concentration, cationic mechanism for the initiation process was favoured[16]. This would apply equally well to the propagation process and, therefore, the initiation by a radical ion mechanism cannot be ruled out[14]. The possibility of proton transfer to monomer leading to decreased average degree of polymerization,similar to conventional cationic mechanism, has also been discussed[12].

The work of Matsumoto et al[15] along with Solomon and Rosser[14] lead to infer that acidity of clay cannot be solely ascribable to either Bronsted acidity or Lewis acidity. It has to be understood that dry mineral surface is very acidic due to the polarisation of residual water molecules by the exchangeable cations. Such acidity is influenced by the solvent as evident from the blue coloration of aqueous benzidine in the presence of oxidized bentonite. Instead a yellow color appeared when a benzene solution of benzidine was treated with dry clay mineral[16,17]. Solomon and Rosser failed to find evidence of styrene interacting with the clay mineral which led to assume that styrene is either incapable of moving into the interlayer space or do so with difficulty.

The polymerization of MMA on such clay minerals has not yet received 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 bentonite complex using the conventional free radical initiator, 2-2'-azobis isobutyramidine AIBA[24]. The polymerization of MMA and methyl acrylate in bentonite interlayer induced by γ-radiation has been studied by Blumstein and co-workers[18-21]. The interlayer polymers were difficult to isolate by the usual solvent extraction and could only be isolated by treating the clay-polymer complex with hydrofluoric acid which damaged most polymers. Glavati et al[22] found that polymerization of acrylonitrile/bentonite 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 bentonite if AIBA was previously introduced to the clay mineral.[23] The cationic form of AIBA goes to the exchange sites in kaolinite and bentonite 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-bentonite complex initiator was greater than that for AIBA alone[24]. It has been proposed that the free radicals remain attached to the adjacent planes of AIBA-bentonite dispersed in water, and on heating, these planes move away from each other allowing more water to penetrate. This can be represented as:

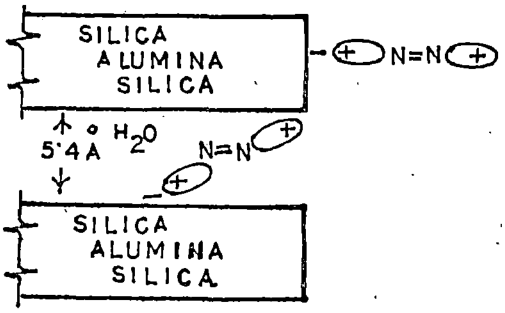


FIG-4

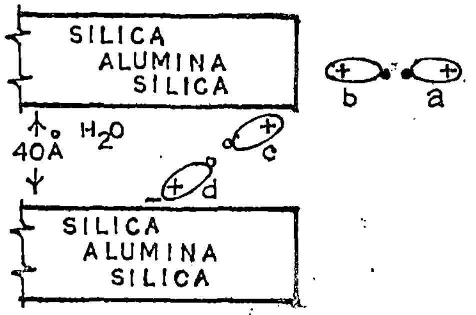
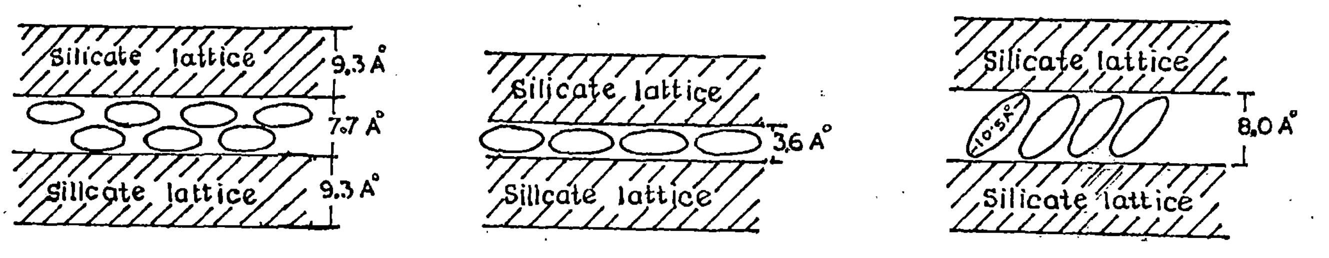


FIG-5

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 by some 30Å, 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. 5) can form homopolymer, and type 'a' radicals are free to be deactivated through recombination with type 'b'. Fig. 5 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-bentonite complex. If the clay is dispersed in methanol, latter surrounds the intercalated free radicals inhibiting their separation and thus facilitating the graft polymer formation.

Solomon and Loft[25] worked with a series of acrylates and methacrylates and, from X-ray data suggested an interlamellar complex formation between monomer and bentonite. This can be illustrated by Fig. 6.



TYPE I

TYPE II

TYPE III

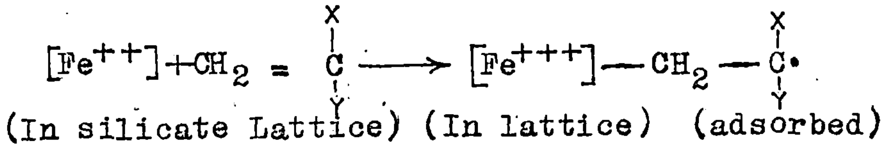
Two monolayers lying flat (spacing shown is for MMA)

One monomer layer lying flat (spacing shown is for dimethyl amino ethyl methaacrylate)

One layer of inclined monomer molecules (spacing shown is for hydroxy ethyl methacrylate)

Fig. 6

Only type III is responsible for spontaneous polymerization of acrylic monomers in presence of a peroxide initiator[25]. 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 initiation, and the propagation involved radical anions. The following mechanisms have been forwarded:



$$[Fe^{++}] + CH_2 = \underset{Y}{\overset{X}{\underset{|}{\overset{|}{C}}}} \longrightarrow [Fe^{+++}] - CH_2 - \underset{Y}{\overset{X}{\underset{|}{\overset{|}{C}}}}\cdot \qquad \text{... (I)}$$

(In silicate Lattice) (In lattice) (adsorbed)

$$[Fe^{++}] + ROOH \longrightarrow [Fe^{+++}] + RO^{\circ} + OH^{-} \qquad \text{... (2)}$$

(In lattice) (In lattice)

Iron is shown as the oxidizable atom in the silicate lattice although other transition metals may be present. In mechanism I 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.

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 polymethylmethacrylate PMMA was 3.68% (Mol. wt. 1.36 x 10^{-6}) whereas with kaolinite and montmorillonite the yields were 0.51% (Mol. wt. 2.81 x 10^{-6}) and 0.68% (Mol. wt. 3.05 x 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 study[30] on the polymerization of vinyl monomers on clay surfaces shows that MMA, vinyl chloride, and acrylonitrile were homopolymerised and co-polymerised with 2-dimethyl amino ethyl 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 tested 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. One more recent work[33] involved ESR study to assess the state of Fe in bentonites. 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 remained unchanged when the cations were altered at the exchanging sites. This indicated that the montmorillonite had practically 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 sulphuric acid concentration provided a measure of the break down of the clay mineral during acid activation.

Studies on the structural properties of the polymers from clay catalysed polymerizations of vinyl monomers have been made by several workers. Blumstein and co-workers[10,18], 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 stereoregularity of this kind could be ascribed to the orientation induced in the intercalated monomer by ion-dipole interactions between the interlayer sodium cations of the bentonite and the ester carbonyl group of the monomer. Earlier, Glavati et al[22] reported to have oriented stereoregular poly(acrylonitrile) and poly (acrylic acid) using similar procedures.

Theng reported[31,32] 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.

A mere recent work[33] reported that PVC or a vinyl acetate vinyl chloride copolymer modified by a latex of Butyl acrylate - Methylmethacrylate copolymer, Butadiene-Styrene copolymer, poly (Methylacrylate) 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, bentonite, or Ca phosphate was added before or during the addition, the polymers with satisfactory particle size separated out from the aqueous suspension.

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