

INTERLAMELLAR SORPTION BY CLAY MINERALS

BY DOUGLAS M. C. MACEWAN *

The term "interlamellar sorption" was proposed by the author in 1948 to designate the penetration of ions and neutral molecules between the layers of a lamellar structure, resulting in a reversible, one-dimensional swelling. The first system of this sort to be studied was graphitic acid (Hofmann et al. 1930), which reversibly takes up layers of water molecules. The phenomenon is mainly met with amongst natural and artificial inorganic substances—in the organic field, a commoner analogous phenomenon is the swelling of polymers by penetration of small molecules between large, chain-shaped molecules, although lamellar systems, in some respects analogous to the inorganic ones, are met with among proteins and soaps.

The interest of the phenomenon is partly due to the light it can throw on adsorptive and surface forces. Alterations in spacing between the layers can very readily be followed by means of X-ray diffraction, since sharp reflexions are given by the sequence of parallel planes. This means that a range of relatively powerful methods is available for studying the size and orientation of the sorbed molecules, and hence the nature of the forces holding them.

Most of the work on interlamellar sorption, especially of organic molecules, has been done using the clay-mineral montmorillonite as substrate, and hence most of this paper will be concerned with this mineral. However, it will be shown that the phenomenon is of fairly frequent occurrence, a number of other suitable substrates being obtainable.

Attention was first directed towards the reversible swelling shown by montmorillonite on sorption of water (Hofmann et al. 1933). It was shown that the spacing of the layers varies (1) with the equilibrium vapor pressure of water; (2) with the exchangeable cations, which are always present in samples of montmorillonite in quantities of the order of 100 me. /100 g. The early results obtained by Nagelschmidt, and by Hofmann and Bilke, appeared to show a continuous change in spacing with water content, but Bradley, Grim, and Clark (1937) obtained evidence for the existence of definite hydrates with definite number of monomolecular sheets of water molecules between the montmorillonite layers. The earlier results can be explained on the basis of the existence of mixed structures, in which, for instance, one-sheet intervals and two-sheet intervals may occur in a random manner. The phenomenon, however, is more complex than Bradley, Grim, and Clark suggested; not only may monomolecular sheets of water molecules occur, but also, as Méring has shown, groupings of water molecules around the interlamellar ions. These questions are being treated in this symposium by Barshad, who has produced much new work in this field. It is an indication of the complexity of the phenomenon that such new work can still be produced, 20 years after the original papers of Hofmann and his collaborators.

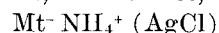
In 1941, Giesekeing and Hendricks showed that the exchangeable cations of montmorillonite may be replaced by large organic cations—amines and polyamines. These

large cations give rise to characteristic spacings between the montmorillonite layers, which may be explained by supposing the organic cations to go between the layers, and in general to lie as nearly as possible flat on the surface of the layers. The ions are of course held to the layers by electrostatic forces, the layers being negatively charged, and the ions positive; Hendricks suggested that van der Waals forces between the uncharged organic groupings and the montmorillonite layers are also of importance, and contribute towards the increased stability of these complexes, as compared with those formed with inorganic cations. Hendricks showed that the observed spacings between the layers are attributable to definite orientations of the large cations, and are compatible with the supposed type of binding between the cations and the layers. In this he broke new ground in the detailed interpretation of inter-layer spacings.

As a logical consequence of Hendrick's postulate regarding binding forces, one would expect neutral molecules of fairly large size also to be strongly adsorbed by montmorillonite, and Bradley (1945) and the present author (1948) have shown that this in fact happens. Apparently any molecule of moderate size, which has a dipole moment may be sorbed, and also certain molecules, like benzene, which have not got a permanent dipole moment. The sorbed molecules do not appear to be in a random arrangement, but form well marked layers, with probably a fairly definite orientation for the molecules composing a layer. The inter-layer spacings observed with different sorbed molecules are thus in principle capable of being fully explained by the orientation and method of binding of the sorbed molecules (MacEwan 1948), though the explanation may not be obvious in any particular case.

These organic molecules are sorbed in neutral form, so the complexes they form are quite different from those with large organic cations, investigated by Hendricks. There are in general three elements in the montmorillonite sorption complex, namely (1) the silicate layers, (2) the interlamellar ions, (3) the interlamellar neutral molecules—water, in the natural mineral. To some extent, either (2) or (3) may be replaced independently of each other.

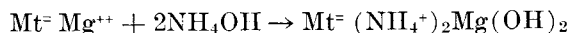
Bloch (1950) has claimed that neutral inorganic molecules may also be sorbed between the layers of montmorillonite. In this case, the inter-layer cations are supposed to be still present, together with molecules such as, for instance, AgCl, giving a complex of the type



where Mt stands for the negatively charged layer of montmorillonite. The NH_4^+ is replaceable by other ions. However, the amount of AgCl appears to be limited to a maximum of one molecule per ion, so the possibility that the AgCl is here forming a component of a complex ion must be considered. This is also suggested by the fact that on replacing the NH_4^+ by Na^+ or Li^+ , complexes of inferior stability are obtained, from which AgCl gradually separates out. The ammonium-saturated complex gives a spacing of 12.6 Å, and does not swell further by imbibition of water.

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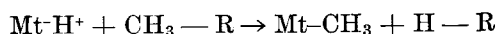
The method by which these complexes are obtained consists in saturation with silver to give $Mt^- Ag^+$, followed by treatment with e.g. NH_4Cl solution. An analogous reaction, giving rise to a product with properties similar to those of the natural chlorites, has been studied by Hémin and Caillère (1949). The treatment consists in saturation of the montmorillonite with Mg^{++} , followed by the application of concentrated NH_4OH solution, giving rise to the probable reaction.



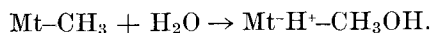
The resulting product, with interlamellar $Mg(OH)_2$, differs, however, from natural chlorites in having NH_4^+ cations present as well.

These reactions raise the question whether free anions can penetrate between the montmorillonite layers. The existing evidence is hardly sufficient to enable an exact mechanism to be postulated for the reactions, but it is possible to formulate both reactions in such a way as to avoid the presence of free anions between the layers.

In the sorption complexes mentioned so far, the interlamellar material is held in two ways, either by electrovalency (ionic exchange), or by residual valencies (dipole and van de Waals forces). Berger (1941), Gieseking (1949), and Deuel et al. (1950, 1952) claim to have prepared a third type of complex in which organic radicals are directly linked to the montmorillonite surface by homopolar bonds. The relationship between this type of complex and the ionic type would be similar to that between dimethyl sulphate $(CH_3)_2SO_4$ and sodium sulphate $(Na^+)_2SO_4^-$. Berger claimed to produce his methyl montmorillonite by reaction of the acid clay with diazomethane:



Deuel (1952) has investigated a number of other methods of introducing organic and other radicals, and claims to have produced methyl and other derivatives of montmorillonite, montmorillonite chloride, methoxy-montmorillonite and numerous other derivatives. The reality of some at least of these derivatives has, however, been questioned by Brown, Green-Kelly and Norrish (1952), on the grounds (among others) that the acid montmorillonite commonly used as a starting material is probably unstable; that the difficulty of obtaining truly dry montmorillonite has been underestimated; and that no adequate evidence based on X-rays has been presented to show that the resulting products are not residual-valency complexes of the type of methanol-montmorillonite. The difficulty of adequate characterization of the complexes is aggravated by the fact that the homopolar derivatives, if they exist, are likely to be highly unstable. Methyl-montmorillonite, for instance, in presence of water, could probably decompose to give methanol-hydrogen-montmorillonite:



Confusion on this question has probably been increased by Berger's original attempt to present the organic reactions as a "proof" for the truth of the Edelman-Favejee structural hypothesis, which postulates the existence of OH groups linked directly to silicon. These reactions are interesting in themselves, but until much

more is known about their mechanism, they cannot be presented as a proof for any structural hypothesis.

In particular, careful X-ray work is needed on well-defined material. At present, no attempt has been made to interpret the few spacing measurements that are available in terms of the dimensions and orientation of the organic groupings allegedly present, nor have any one-dimensional fourier syntheses been made from X-ray data. If well-defined complexes do indeed exist, then both things should be possible. At present, the existence of these complexes is possible, but not conclusively proved. If, however, they really exist, then they would open up a most exciting new method for the study of organic reactions, since a big variety of such reactions involving organic radicals could be reproduced on the surface of montmorillonite, and their progress studied directly by X-ray diffraction.

Methods of Study of Interlamellar Sorption Complexes. The X-ray diffraction method is at present the most valuable technique for characterizing interlamellar sorption complexes. The simplest measurement one can make by its means is that of the (001) spacing, derived by measurements of the inner reflexion of the X-ray diffraction diagrams. A considerable amount can be deduced from this measurement alone if comparison is made between several related complexes. These may result from variation of any of the several factors involved in the formation of these complexes—sizes of the molecule, the nature of the interlamellar cations, the amount of sorbed material, etc.

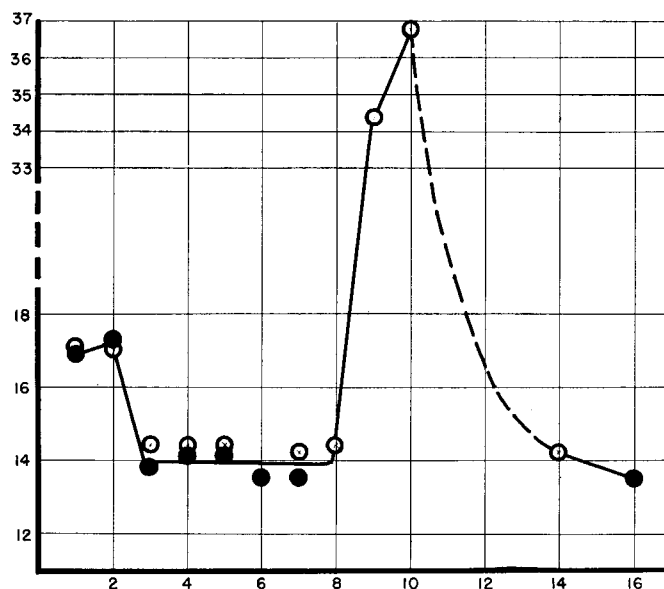


FIGURE 1. Variation of basal spacing with chain length, for complexes of Ca-montmorillonite, with monohydric alcohols, from data of MacEwan (1948) (open circles) and Barshad (1952) (black circles).

As an example, two plots are shown illustrating the variation of (001) spacing with chain length of absorbed organic molecules, derived from results obtained by MacEwan (1948, 1946), Barshad (1952) and Jordan (1949). In the first diagram (fig. 1) the adsorbed molecules are alcohols and therefore neutral: in the second

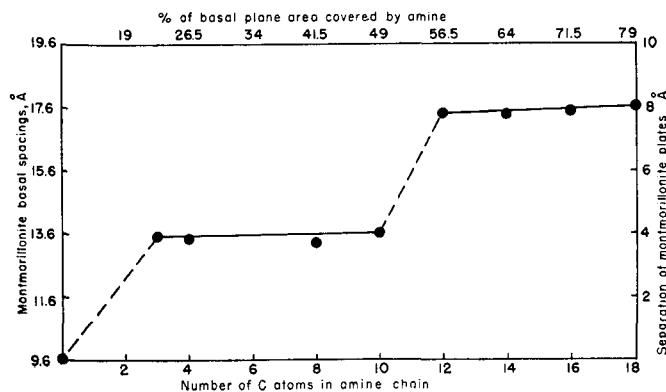


FIGURE 2. Variation of basal spacing with chain length for complexes of montmorillonite with straight-chain amines, from Jordan's data (1949).

(fig. 2), they are amines, and present in the form of positive ions. These graphs at once suggest two things: (a) the spacings do not vary continuously, but alter in jumps, so that sheets of molecules are probably present; (b) if we subtract the thickness of the montmorillonite layers, the larger spacing is in each case about twice the smaller one, so that single and double thicknesses of molecules are probably present in the two cases. Further, the actual value of the space available for the molecular sheets suggests that in each case the molecules are lying as flat as possible on the montmorillonite surface.

Further, it will be noted that in the first graph the spacing initially goes up with increasing number of carbon atoms, and in the second it goes down. This straightaway suggests a different mechanism for adsorption in the two cases. In the first case, the number of

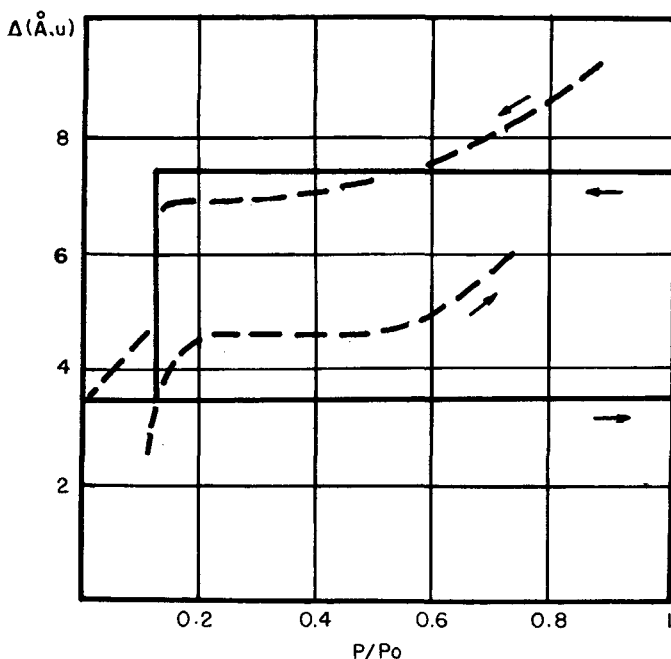


FIGURE 3. Variation of spacing ($\Delta = d_{001} - 9.4\text{\AA}$) with partial pressure of acetone vapor in contact with Ca-montmorillonite, for increasing and decreasing vapor pressures, as indicated by arrows. The dotted lines give the corresponding sorption isotherms. From Glaeser (1950).

layers is determined by the energy of adsorption, and this goes down as the non-polar part of the molecule becomes bigger; in the second, the number of layers present depends on the space occupied by a quantity of molecules sufficient to balance the charge on the montmorillonite surface.

Still more detailed suppositions can be made, with a rather smaller degree of conviction. Thus for the alcohols, it is observed that there is a slight increase in spacing from methanol to ethanol, and a similar increase is observed with the glycols (Bradley, 1945). The author has attributed this to the influence of the more intense binding of the α -carbon atoms to the montmorillonite surface, as compared with the other carbon atoms in the chain (a conception which was formulated by Bradley).

Barshad (1952) has recently found very high spacings with nonanol and decanol, and these are shown on the graph. They must correspond to a molecular rearrangement, the exact nature of which is not at present clear.

The (001) spacing may be plotted against other variables. It may for instance be plotted against the partial vapor pressure of the adsorbed substance, and in this way compared directly with adsorption isotherms. Figures 3 and 4 show two plots of this type, taken from results obtained by Miss Glaeser (1950), for acetone adsorption by calcium and sodium montmorillonites. The dotted lines show the corresponding adsorption isotherm measurements. In each case two spacings are observed. With the desorption isotherm of the Ca-montmorillonite the transition from $\Delta = 7.4\text{\AA}$ to $\Delta = 3.5\text{\AA}$ is sharp, and this corresponds to a sudden drop in the desorption isotherm. In the case of the Na-montmorillonite a region of mixed spacings is formed between $\Delta = 8.8\text{\AA}$ and

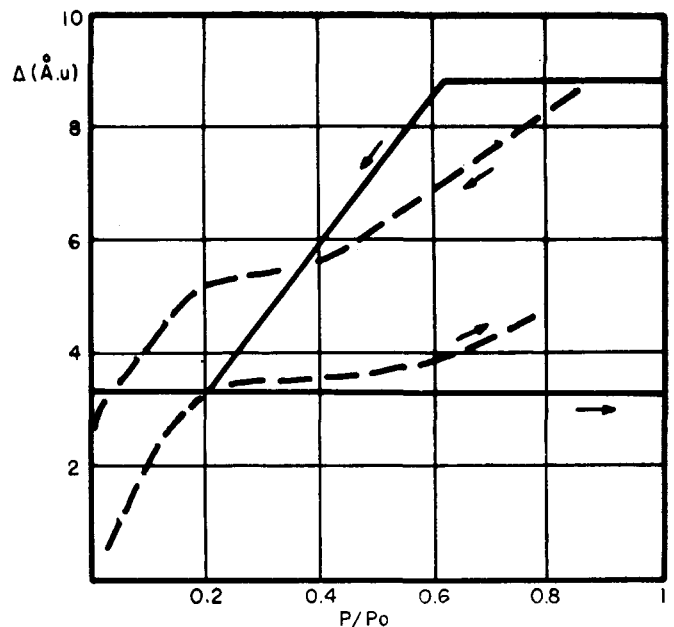


FIGURE 4. Variation of spacing ($\Delta = d_{001} - 9.4\text{\AA}$) with partial pressure of acetone vapor in contact with Na-montmorillonite, for increasing and decreasing vapor pressures, as indicated by arrows. The dotted lines give the corresponding sorption isotherms. From Glaeser (1950).

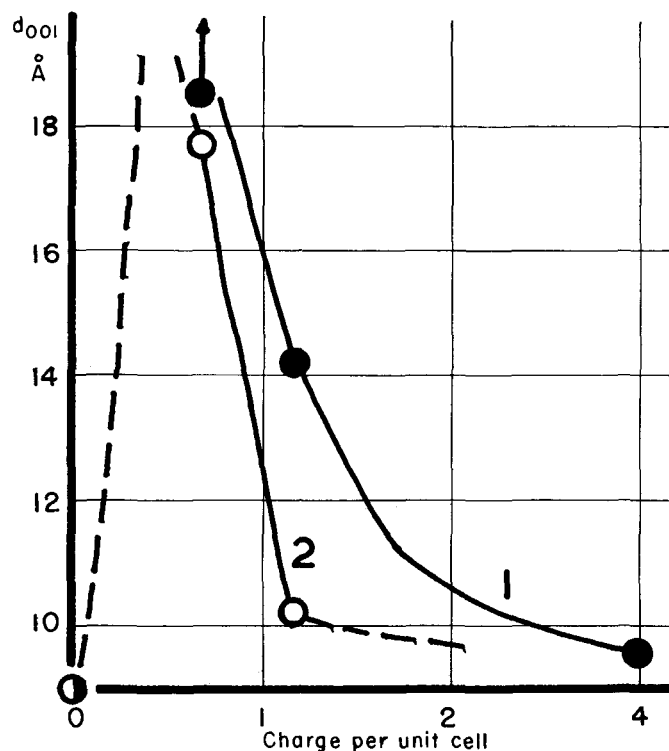


FIGURE 5. Basal spacing as a function of charge on the layer, for Ca^{++} -water-saturated minerals (black circles) and Na^{+} -glycerol-saturated minerals (open circles). From data of Mering, MacEwan, and Barshad. Actual minerals represented in this graph are pyrophyllite (charge 0); montmorillonite (charge about $\frac{3}{4}$ unit per unit cell); vermiculite (charge 1 to $1\frac{1}{3}$ units per unit cell); mica (charge 4 units per unit cell). The actual degree of expansion varies with the exchange cations and neutral molecules present, but the general tendency is towards the sort of curve shown with a region of high maximum expansion, and no expansion for either very low or high charge.

$\Delta = 3.3 \text{ \AA}$ and this corresponds to a gradual drop in the desorption isotherm.

The value $\Delta = 7.4$ is sufficiently near to 2×3.5 to make it likely that the two spacings observed with the Ca-montmorillonite correspond to structures with one and two layers of acetone molecules respectively. The value $\Delta = 8.8 \text{ \AA}$ observed with the Na-montmorillonite however probably corresponds to a different molecular arrangement.

The hysteresis which is shown by the adsorption and desorption isotherm is reflected in the (001) spacings. Certain other features of the adsorption and desorption isotherms have no direct correspondence in the X-ray spacing plots. It is clear, however, that these provide valuable additional information in conjunction with the isotherm data.

It would be instructive to plot a graph showing the variation of spacing with charge on the layer. The last-mentioned quantity is of course a constant, not susceptible of experimental variation, but it is possible to find a range of minerals of similar structural type, and with different charges on the layer. In making a comparison, of course, all the other factors, in particular the interlamellar cations and sorbed molecules, must be kept constant, and it is therefore difficult to assemble a

set of comparable data. The graphs in fig. 5 are based on data for five mineral types—pyrophyllite with zero, or near zero, charge on the layer, which shows no expansion without special treatment (Caillère and Hémin, 1950); montmorillonite with a charge of about $\frac{3}{4}$ unit per unit cell layer; vermiculite with a charge of about 1 unit to $1\frac{1}{3}$ units; mica with 2 units; and brittle micas with 4. The last-mentioned group also shows no expansion.

The graphs show a clear tendency for the expansion to rise to a maximum at a charge near to that of montmorillonite, and fall away for higher charges. The maximum may however occur at lower charges than that of montmorillonite, since the corresponding minerals are not available. There is therefore probably an optimum charge for interlamellar expansion, and this may be near to the charge of montmorillonite. Barshad, in his contribution to this series of papers, gives some consideration to the implications of this fact.

We have so far been concerned with what can be learned by a consideration of the (001) spacings only. More information can be obtained when the whole sequence of (001) reflexions is taken into account. This may at the very least serve to draw attention to the cases where the apparent (001) reflexion does not represent a true spacing, but results from a mixed structure of two or more spacings. If a true single spacing is present, the higher-order reflexions will occur at integral sub-multiples of this, of the form d , $d/2$, $d/3$ etc. If the reflexions do not form a rational series of orders, then a mixture of spacings is present, and special methods are required for the interpretation of the diagram.

If a single spacing is indeed present, it is possible to perform a one-dimensional fourier synthesis, using the measured spacings and intensities of the series of basal reflexions. Bradley (1945) has shown that even a rough estimate of the sequence of intensities may enable a distinction to be made between two-layer and three-layer structures. We have been trying to improve on this result by increasing the number of available intensities, and the accuracy of their measurement. A small oriented flake of the treated montmorillonite is used, and a series

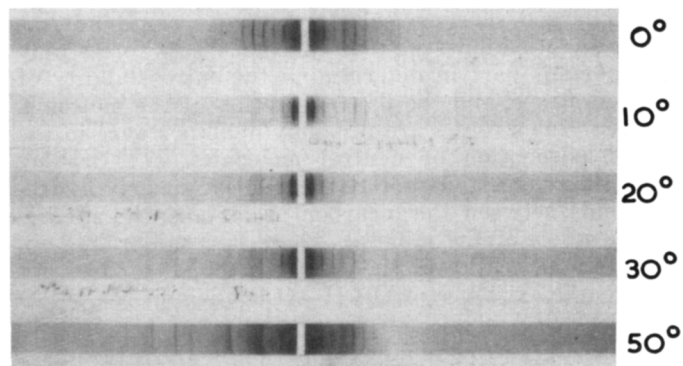


FIGURE 6. X-ray diagrams of a glycerol-montmorillonite flake, with the flake set at different angles to the axis of the X-ray beam (indicated on the right). The flake was turned towards the right: note that on this side the higher orders of the basal reflexions appear as the angle of turning is increased. At the same time, on the other side, general hk reflexions appear and the basal reflexions diminish in intensity.

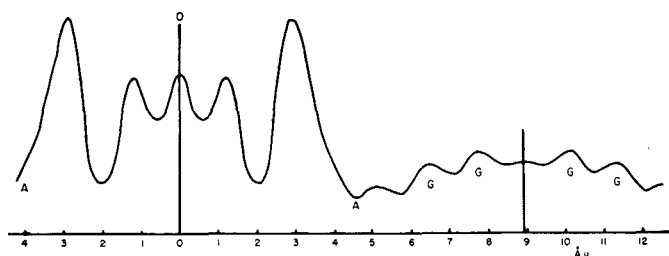


FIGURE 7. One-dimensional Fourier synthesis of Tl^+ -glycerol-montmorillonite. This diagram covers about one whole repeat distance (17.7\AA). There are centres of symmetry at O and B, and about these two points the diagram repeats itself. The portion AA represents the silicate sheet, and is about the same for all the montmorillonite complexes. The probable significance of the peak in this region is indicated. The peaks marked G are probably due to glycerol molecules, and the small peak above the numeral 9 to the Tl^+ exchangeable cations.

of diffraction diagrams is recorded, with the flake set at different angles to the beam.

Figure 6 shows a set of such diagrams for glycerol-treated montmorillonite, obtained by G. Brown (1950). It is possible from such a set to plot a curve showing intensity of reflexion as a function of orientation, and thus to eliminate the effect of preferred orientation, though certain complicating factors, especially absorption in the specimen, have to be allowed for.

To certain extent direct methods may be used for determining the phase of the reflexions, so that the degree of ambiguity is relatively small. The difficulty arises in interpreting the features observed in the Fourier diagrams.

Figure 7 shows a Fourier synthesis obtained from a glycerol-montmorillonite, with Tl^+ as exchange cation (Brown, 1950). The part on the left up to the point marked A is a universal feature of the montmorillonite curves, and corresponds to the silicate layer. The rest of the diagram represents the material between the layers—glycerol molecules, and Tl^+ and other cations. There is reason for believing that the peak marked B corresponds to the Tl^+ ions.

Mechanism of Interlamellar Sorption. The sorption of large complex ions may be ascribed to an ordinary cation-exchange process, the ions being held to the negatively charged sheets by electrostatic forces. Hendricks (1941) suggests however that van der Waals forces play an important part in determining the extra stability of such complexes, and the flat orientation of the molecule. Van der Waals forces are probably of importance in the case of adsorption of neutral molecules, but Bradley (1945) has suggested another mechanism, namely hydrogen bonds between the α -carbon atoms and the surface oxygen atoms of the mineral. There is considerable evidence for the reality of such a bond, though it does not rule out the existence of $\text{O}-\text{H}-\text{O}$ bonds and $\text{N}-\text{H}-\text{O}$ bonds as well.

These forces provide an explanation of the attachment of neutral molecules to the sheets, and therefore of the repulsion between them. The balancing attractive force may be partly electrostatic in character, and partly van der Waals attraction between neighboring layers, but the electrostatic force appears to be the only adequate one at short distances. We have recently been making

calculations on the probable variation of the electrostatic attractive potential with distance, and find that, as one would expect, it dies off very rapidly for a surface with high charge density, less rapidly for one with low charge density (fig. 8). At separations of the order of 100\AA or so, the Gouy layer repulsion and van der Waals attraction may be the only forces of importance. It follows from this work that a suitable value of the surface charge density is essential for these inter-

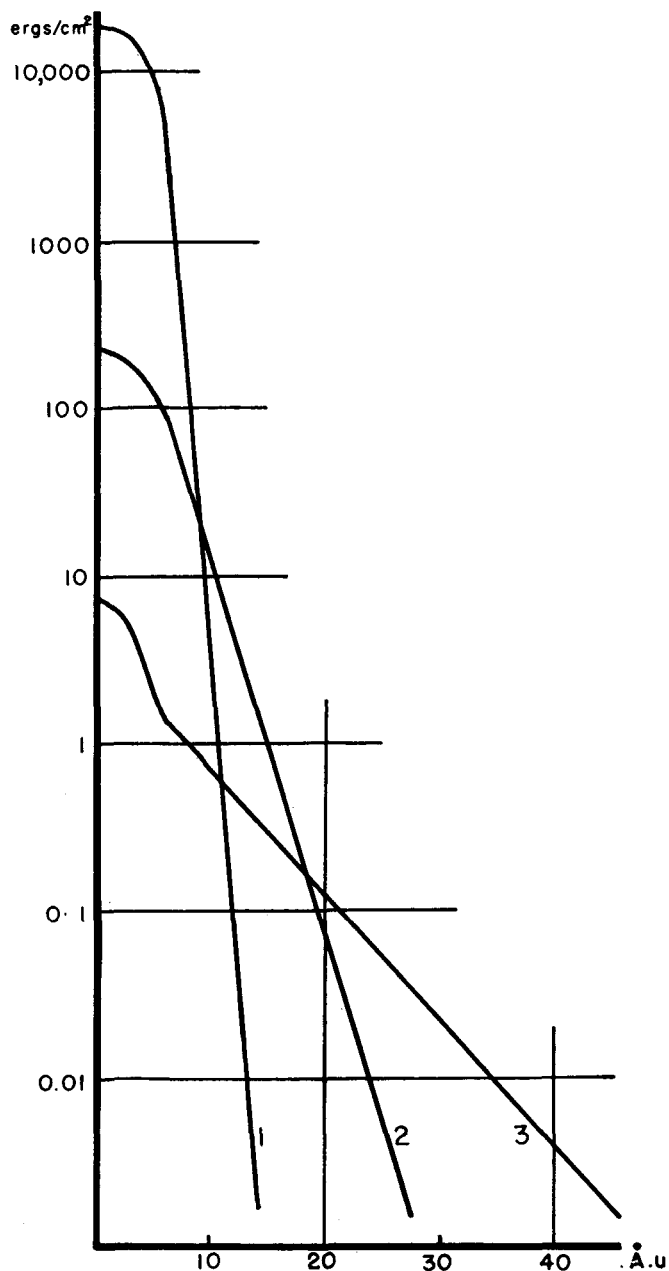


FIGURE 8. Potential energy of the configuration (charged sheet)-ions-(charged sheet) as a function of distance between opposite surfaces of the sheets. Curve 1 refers to a sheet having ten times the surface density of charge of montmorillonite; curve 2 to montmorillonite; and curve 3 to a sheet having one-tenth the surface density of charge of montmorillonite. Any calculation such as this depends of course on a number of assumptions, which cannot all be specified here.

lamellar adsorption complexes to be formed. If the surface charge density is too high, the attractive force will not manifest itself except at very close distances. If the surface charge density is too low, the attractive force will be effective at fairly large distances, but will not be large enough to equilibrate the repulsive force at any distance.

In this case, there will however be a position of equilibrium for very close approach in which the van der Waals attractive force is balanced by Born repulsion. This is the only type of equilibrium for close approach which is recognized by Verwey and Overbeek (1948) who do not postulate either an adsorption-repulsion, or a short-range electrostatic attraction.

A complicating factor which must be taken into account is that the interlamellar molecules interact with the exchange cations as well as with the clay-mineral surface. This is clearly shown by the fact that the number of sheets of certain organic liquids which penetrate between the montmorillonite layers is dependent on the exchangeable cation, and may differ even for two cations of the same size.

It seems likely that this type of short-range equilibrium is of general occurrence when charged surfaces are brought together in a liquid medium, and therefore that it ought to be taken into account in explaining colloidal phenomena. The forces considered here are additional, and not alternative, to those considered by Verwey and Overbeek in their book *Theory of the Stability of Lyophobic Colloids*.

Interlamellar Sorption by Other Materials. The phenomenon of interlamellar sorption is not characteristic of montmorillonite alone. A range of materials shows an essentially similar behavior, though for most of them

the details of the process have not yet been investigated. Graphitic acid was in fact studied by Hofmann earlier than montmorillonite, and it shows a very similar swelling with water, though there is no report of its interaction with organic liquids. At Rothamsted, we have studied α -zinc hydroxide (MacEwan and Talibudeen 1949), a system which shows a complicated type of adsorption. Apparently the hydroxide surface first covers itself with a double layer of negatively charged dye molecules, and neutral organic molecules are then taken up between these (fig. 9). It is not known whether positive ions are present, though this seems probable.

We have also studied the halloysite system. It is still however, uncertain whether the adsorption of organic molecules is in this case analogous to that by montmorillonite, i.e., whether exchangeable ions play a part. A large cation-exchange capacity has been reported for halloysite by Rivière (1950), but this is in conflict with the findings of other workers.

The hydrated calcium phosphate, autunite has been investigated here by G. Brown. This shows reversible interlamellar sorption of water, but the organic liquids we have tried, while effective in removing water, are not themselves sorbed.

Hénin and his collaborators (1950) have recently been doing some very interesting research on a number of materials having layer structures, and have found that many of them will show interlamellar sorption of water after suitable treatment. The materials for which the phenomenon has been demonstrated are hydrargillite, bayerite, brucite, barite, antigorite, and nouméite. The range of materials showing interlamellar sorption has thus been greatly extended, but this work can only be regarded as preliminary in character, and a good deal of additional research will be needed to clarify what is happening as a result of the treatments used.

For the sake of completeness, one ought perhaps to mention the reversible swelling of protein crystals by penetration of layers of water, as observed by Perutz and others (1947), and the lamellar soap systems studied by McBain (McBain and Marsden 1948) although these systems may not be analogous to the ones just mentioned.

Proteins also form complexes, of the ionic type, with montmorillonite, and these have been studied in our laboratories by O. Talibudeen (1950), who found that a structure is readily formed in which the protein molecules appear to be fully stretched out on the surface of the montmorillonite sheets, giving a relatively low spacing of about 18 Å.

DISCUSSION

W. T. Cardwell, Jr.:

There are great differences between different montmorillonites. Some swell no more than kaolinite, so it seems meaningless merely to say that a sample is montmorillonite. I would like to hear more about the differences between montmorillonites.

M. D. Foster:

Among 12 samples of montmorillonite that I have studied, from different localities in the United States and Mexico, three-fold differences in macroscopic swelling were found. No correlation was found between exchange capacity and swelling but correlation was found between substitution in the octahedral group of the structure and swelling. In this respect ferric Fe, although it does not affect the charge, had as much influence as Mg. Three of the samples, having the same tetrahedral charge and the same Mg substitution,

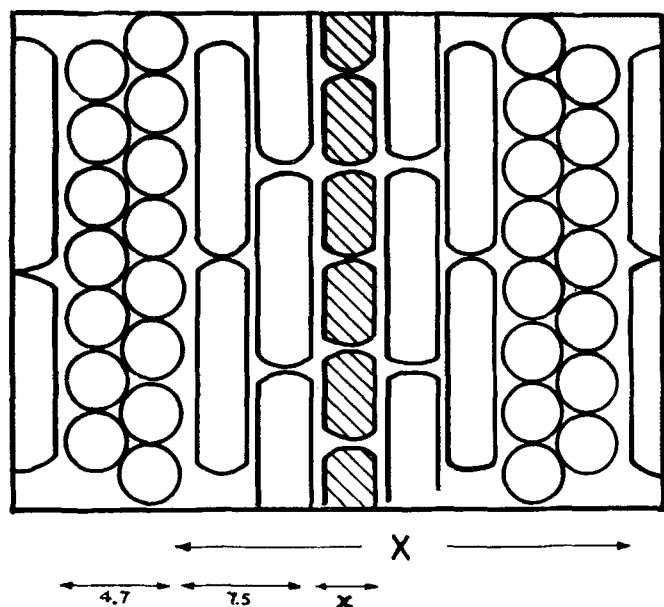


FIGURE 9. Hypothetical structure of the α zinc hydroxide-naphthol yellow complexes with neutral organic molecules, according to Talibudeen and MacEwan (1949). The double rows of circles represent the zinc hydroxide layers, the long flat molecules are the dyestuff, and the small shaded molecules are the neutral substance.

but containing different amounts of ferric Fe, ranged from 21 to 43 mm per gram in swelling capacity. Two other samples had the same composition and the same total Fe content but differed in the state of oxidation of the Fe. The sample with 2/3 ferrous Fe and 1/3 ferric Fe swelled only two-thirds as much as the sample with 2/3 ferric and 1/3 ferrous Fe. Thus chemical composition must be considered in arriving at an interpretation of the relative swelling of different samples of montmorillonite.

G. W. Brindley:

From what Dr. Foster has said it appears that we may have to distinguish between two kinds of swelling in montmorillonite; swelling that results from water penetrating between layers and swelling arising from water between particles. In the former there would be regularly spaced layers; in the latter the particles would have various orientations with respect to one another. Barshad emphasized that in regard to the swelling of montmorillonite in water vapor, the factors of importance are the charge on the layers and the size and charge of the interlayer cations. It might appear that Dr. Foster's results were inconsistent with Barshad's views, but she was dealing with Na-montmorillonite in the presence, not of water vapor, but of a considerable excess of liquid water. There is therefore no conflict.

It is of interest that Méring has shown that Na-montmorillonite placed in water swells to such an extent that the basal spacing increases up to 20 Å. Beyond that it is difficult to follow. The structure swells to the point where there are individual sheets of montmorillonite with no spatial regularity between them (Méring 1946). The situation then would be quite different from that referred to by Barshad. Would Dr. Foster state the conditions of her experiments in view of the possibility of the different mechanisms of the swelling?

M. D. Foster:

One gram of air-dried Na-montmorillonite was ground to pass a 20-mesh sieve, then dropped a few particles at a time into a cylinder containing water. Five minutes later, when it was assumed that these particles had come in complete contact with water, a few more were added. This was repeated until all the sample had been introduced into the cylinder. The cylinder was then allowed to stand 24 hours and the height of the clay in the cylinder read.

D. M. C. MacEwan:

I feel very doubtful whether Na-montmorillonite layers are randomly dispersed when it is fully swollen. K. Norrish (1954), at Rothamsted, has been making experiments with swollen systems: with the highest degree of swelling observable in a very dilute NaCl solution there was still orientation. In that condition the spacing between layers was about 120 Å. I have considered the question of the degree of disorientation of neighboring layers and the curvature that are compatible with good X-ray patterns. Both appear to be small. Thus, in highly swollen Na-systems the layers may still be oriented parallel to each other.

R. A. Rowland:

What is the distinction between the two kinds of swelling?

D. M. C. MacEwan:

Norrish's experiments were made on a Na-system. The material placed in plastic tubes was thoroughly leached with chloride solutions of different concentrations. Plotting the $d(001)$ spacings against concentration he found that the spacings go up to about 20 Å with decreasing concentrations. But at about 20 Å the spacings become broader and weaker until at considerably less concentration a spacing of about 35 Å appears and this increases with decreasing concentration up to about 100 Å. It appears that at certain concentrations there are mixed structures with both high and low spacings simultaneously present. At about 20 Å the layers seem to separate layer from layer to a new equilibrium position at considerably higher dilution. We have considered possible explanations for this, but as yet have found none that is entirely satisfactory.

W. T. Cardwell:

In the suspension where a spacing of about 100 Å was reported, were the layers still parallel in the suspension, were they merely oscillating at random, or was it a matter of an average distance?

D. M. C. MacEwan:

The layers of montmorillonite must have been rather well oriented parallel to one another, in order to account for the observed diffraction effects.

I. Barshad:

In regard to Rowland's question as to where intramicellar swelling ends and intermicellar swelling begins—it depends on how the experiment is made. Starting with a dry Ca-system and using water vapor, intramicellar swelling seems to end with a relative humidity of about 50 to 60 percent, but in the presence of liquid water intermicellar swelling also takes place. In other words, liquid water appears to be essential for intermicellar swelling.

R. A. Rowland:

In the dry state there are outside surfaces and many more inside surfaces. Upon swelling to about 20 Å, surfaces that were inside surfaces become outside surfaces. There is, then, a discontinuity in the X-ray pattern and a change in chemical behavior, either gradual or slight. I do not believe there is any justification for the distinction made between inside and outside surfaces unless it can be demonstrated that the inside surfaces take new properties upon becoming exposed. The effect is probably due to distance from the surface, and the designation of inside and outside is confusing.

M. Soldate:

In the literature, at least by implication, there is the statement that certain illites swell (Hughes and Pfister 1947). Is this a case of intralamellar swelling in which the spacings change?

P. G. Nahin:

Graphic illustrations are given in the literature showing that the settling volumes of montmorillonite, illite, and kaolinite diminish in that order. From our experience it seems that one reason why Na-illite swells less than Na-montmorillonite is that the mechanical and chemical forces that hold the layers of illite together are too strong to permit water to enter between layers.

R. C. Mielenz:

It is well known that montmorillonite-type clay, and some illite types, produce large swelling pressures. As measured in our laboratory, undisturbed montmorillonite-type soils containing small amounts of illite and kaolinite produce swelling pressures as high as 200 psi. Jennings (1950) reported experience in South Africa with soil which developed a swelling Ca-illite pressure of 3.5 tons per sq. ft. I wonder to what extent osmotic forces are involved here.

W. F. Bradley:

The epitactic arrangement of water molecules in the hydration layers on a montmorillonite surface is sufficiently similar to their arrangement in ice, particularly in the property of density, that the swelling phenomenon is quite analogous to freezing, and pressures developed in the two processes are analogous.

E. C. Henry:

The hydration of dehydrated clay particles can be followed by measuring the heat of wetting or by measuring the energy involved in dehydration in differential thermal analysis (Siefert and Henry 1947). By both methods our results agree well with those of Hendricks who found that both the hydration of specific cations and the wetting of surfaces are involved.

C. G. Dodd:

What is the relation of water adsorption to the three structures of montmorillonite as proposed by Hofmann, Endell, and Wilm; Edelman and Favejee; and McConnell (1951)?

Duncan McConnell:

As was pointed out recently by Mackenzie (1951), the structure proposed by myself may be looked on as a compromise between the other two insofar as the dimension of the c -axis and the exposed hydrogens are concerned. I believe that we are not able to distinguish between the Edelman structure and mine on the basis of base-exchange capacity or swelling properties, except that Edelman's structure will not provide for sufficient contraction accompanying complete removal of low-temperature water.

D. M. C. MacEwan:

I am not sure if McConnell proposes that the OH ions which he postulates as replacing O ions on the surface of the montmorillonite layers should be capable of dissociating protons, and thereby contributing to the cation exchange. However, if this process takes place, then after dissociation, the structure is indistinguishable from the Hofmann one. Of course, this comment does not apply to the $(OH)_4$ groups which McConnell also postulates.

D. McConnell:

The difference would be that in my structure there would be certain tetrahedral positions without Si^{++++} or Al^{+++} ions, whereas all such positions are assumed to be filled in Hofmann's structure.

E. A. Hauser:

What type of montmorillonite was used in the experiments with the Ag^+ ion that were referred to in MacEwan's paper? In the equations, Ag-montmorillonite to which NH_4Cl was added was represented as giving rise to montmorillonite- $\text{AgCl}\cdot\text{NH}_4$; this from the point of view of colloid chemistry, is difficult to understand, because the Ag^+ ion is the counter ion and not unionized as an AgCl molecule.

D. M. C. MacEwan:

The work in question was done by Bloch (1950), and I was of course merely reporting it. The montmorillonite used was described as "Terre de Taourirt" from French Morocco, obtained from the "Société française des Glycérines." For the reactions described, the starting material was Na-montmorillonite, obtained by reaction between the electrolysed product and NaOH . This was treated with an excess of AgNO_3 (3 percent) to give a Ag-montmorillonite, and the latter was treated with a 10 percent solution of NH_4Cl , and washed. This is presumed to result in an NH_4 -montmorillonite, and AgCl , the latter being left between the layers rather than being precipitated out in the free solution. The same kind of decomposition has been carried out by Bloch with a number of other substances. In some cases where insoluble compounds are left between layers, a separate phase gradually forms as a result of aging.

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