# INTERLAMELLAR REACTIONS OF CLAYS AND OTHER SUBSTANCES

*by*

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## ABSTRACT

This paper reviews the present state of knowledge on clay mineral complexes and its theoretical and practical importance. It contains a plea for placing the study of these complexes in the more general context of interlamellar sorption in crystalline materials.

## INTRODUCTION

Table 1 gives a list of the types of complex formed by clays. Most clays which are capable of complex formation contain, in their natural state,

TABLE 1.—TYPES OF COMPLEX FORMED BY CLAYS

| Cation | Neutral Molecule | Complex | Investigators |
|---|---|---|---|
| Inorganic | Water | Clays in natural state and base-exchanged | Numerous investigators |
| | Long chain inorganic | α-complexes β-complexes | Bradley, MacEwan, etc. Barshad; Hofmann, Weiss and coll.; MacEwan and coll. |
| | Aromatic, etc. | | Greene-Kelly, etc. |
| | Inorganic salt | Bloch complexes | Bloch |
| Organic | Water (or nothing) | Can also be divided into α- and β-complexes | Hendricks, Jordan, etc. |
| | Organic | | Greene-Kelly, Weiss |
| | Inorganic salt | ? | ? |
| | Halloysite complexes (no cations) | | |
| | Water | Halloysite in natural state | Numerous investigators |
| | Organic | Halloysite–organic | MacEwan, etc. |
| | Inorganic salt | Halloysite–salt | Wada, Walker, Weiss |
| | Inorganic salt + organic molecules | ? | ? |

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interlamellar cations and water. Complex formation can occur essentially in two ways. The first—discovered by Hendricks (1941)—consists in re- placement of the cations by large organic cations. The second—discovered by Bradley (1945) and myself (MacEwan, 1944, 1948)—consists in replace- ment of the water by neutral molecules. These are generally polar organic molecules but may be inorganic salts, as in the types of complex discovered by Bloch (1950). In the table, I have ventured to introduce the name "Bloch complexes"—a convenient name, and justifiable, I think, since all the work on this type or complex has so far been done by Bloch.

We have introduced here a slight broadening of the range of discourse. This symposium is entitled "Clay–Organic Complexes." I feel nonetheless it would be artificial to exclude from consideration the complexes with inorganic salt. It just happens that interest has been focused on complexes in which one of the elements is organic.

The complexes of halloysite may well form a separate category, having no interlamellar cations. We will return to this question later.

I am concerned here entirely with the interlamellar type of complex, which is my own particular interest, although other types of complex are formed by clays. A certain number of papers has been published on organic complexes of attapulgite and sepiolite, which are potentially important, but are more difficult to investigate experimentally. The same applies to the surface sorption complexes. In fact, most of the scientific and practical work is concerned with the interlamellar type of clay complex.

The scope of this work is indicated in Table 2. Here I have indicated the main current lines of research on interlamellar complexes.

Table 1 suggests at once the possibilities of types of complex that have not yet been investigated. It may be possible to form Bloch complexes in which the cation is organic instead of inorganic. Admittedly there is some evidence to suggest that the Bloch complexes are fundamentally cation–salt associations rather than clay–salt associations, and this may make it difficult or impossible to form them with organic cations.

There is also (at the time of writing) no published work on mixed com- plexes of halloysite with inorganic salt and neutral organic molecules. Here again their existence does not seem to be excluded *a priori*.

It will be desirable perhaps to discuss Table 2 point by point, parti- cularly as the papers presented at this meeting belong to a rather limited range of types. Most of them, in fact, are of classes 1a, or 2a (i). I would like to take this opportunity therefore of pleading for an extension of this work to cover a wider range of types of problem.

Class 1a need not be elaborated on. It is the field of the classical work on clay complexes by Hendricks, Bradley and MacEwan. Recent work in this field has been done by Greene-Kelly (1954, 1956), Greenland (1956) and

Weiss, Mehler and Hofmann (1956). The number of papers belonging to this class which are being presented at this conference shows that it is far from being exhausted.

TABLE 2.—CURRENT LINES OF RESEARCH ON INTERLAMELLAR COMPLEXES

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1. *Studies of molecular orientation and binding forces*
   a. With pure substances
   b. With mixtures of substances

2. *Physico-chemical studies*
   a. Sorption isotherms (i) in solution; (ii) in vapor phase
   b. Swelling in electrolytes—long range forces—passage from two-dimensional to normal liquid
   c. Rates of migration of sorbed molecules on surface
   d. Production of molecular sieves of controllable widths
   e. Viscosity studies

3. *Chemical studies*
   a. Chemical modification of layer surface
   b. Modification of chemical reactions in interlamellar space

4. *Crystallographic studies*
   a. Studies of crystalline disorder
   b. Studies of phase changes in two-dimensional films

5. *Mineralogical studies*
   a. Problems of mineral identification: indirect estimation of charge density on layer; determination of hydratable surface by sorption

6. *Biological studies*
   a. Modification of enzymatic and bacterial decomposition of sorbed molecules

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Class 1 b I suggest, would warrant much more study. When molecules are mixed in two-dimensional films, they do not arrange themselves randomly. On the contrary, they take up patterns which are of considerable interest, and may be quite complex (as in the water–acetone mixtures studied by Ruiz Amil and MacEwan, 1957). Further examples will be mentioned later.

Several papers from class 2 a (i) are being presented to this meeting. Class 2 a (ii) has seen important contributions by Greene-Kelly, Glaeser (1954) and Gutierrez Rios and collaborators. Class 2 b, is represented at this meeting by Walker's paper. It is potentially of enormous importance, for the light it may cast on colloidal forces. Class 2 c, is represented by Walker's work on diffusion in vermiculite. Class 2 d, is represented by the work of Barrer and collaborators on alkyl-ammonium clays. Class 2 e, is represented here by van der Watt and Bodman's paper.

Of class 3a the only representatives at this meeting are concerned with cation exchange reactions (*e.g.* Cowan and White's paper). The homopolar complexes of clays introduced by Deuel (1952) have been more or less neglected recently, since numerous difficulties have been pointed out (Brown, Greene-Kelly and Norrish, 1952; Greenland and Russell, 1955; Schwarz and Hennicke, 1956); but a recent paper by Barrer and Reay (1958) makes it clear that we might be over-hasty in jumping to the conclusion that genuine complexes do not exist.

Class 4b represents a category of research which has been very generally neglected, until Weiss showed its possible importance. Table 3 is taken from

TABLE 3.—INFLUENCE OF THE DEGREE OF SWELLING OF MONTMORILLONITE
ON THE CATALYTIC OXIDATION OF *p*-PHENYLENEDIAMINE

| Na-montmorillonite Suspended in | Interlayer Distance (Å) | Color of the Montmorillonite + *p*-Phenylenediamine after 3 hr |
|---|---|---|
| Distilled water | ∞ | Yellowish |
| 0.01 N NaCl | ∞ | Yellowish, tinge of green |
| 1.0 N NaCl | 19.2 | Blue |
| 3.0 N NaCl | 16.0 | Deep blue |
| ca. 5.0 N NaCl | 15.2–15.7 (nonuniform) | Black |

(Weiss, 1958.)

Weiss (1958), and shows the dependence of the catalytic oxidation of *p*-phenylenediamine by the oxygen of the air on the state of swelling of the montmorillonite in which it is sorbed. Dr. Pinck's paper to this Conference may be regarded as belonging partly to this class.

Interlamellar complexes afford considerable scope for crystallographic studies of disorder (class 4a). This is a study which has been commenced by my collaborator, Mr. H. H. Sutherland. Topic 4b has been little studied (MacEwan and Aragon, 1959), but might be capable of considerable development.

Numerous papers have been published on mineral identification using complexes—class 5a (MacEwan, 1946; White and Jackson, 1946; Mehra and Jackson, 1959; Greene-Kelly, 1952; Walker, 1958, 1959; Dyal and Hendricks, 1950). The recent salt-complexing technique for identification of kaolinite, introduced by Wada and Jackson, is a notable step forward, particularly interesting as it represents the first application of an inorganic complex in this field.

Group 6a is represented by Dr. Pinck's paper at this Congress—an isolated representative of a field of study which offers considerable possibilities.

## INTERLAMELLAR SWELLING

I would like to draw attention here to an important paper by Weiss (1958) in which the links between interlamellar swelling and colloidal phenomena are emphasized.

Weiss draws attention, in particular, to the importance of the charge on the layer in determining swelling behavior: "The swelling properties depend in the first place on the number of charges per unit of surface." This point was emphasized by the present author in his contribution to

TABLE 4.—DEPENDENCE OF INTERLAYER SWELLING ON THE RECIPROCAL OF THE SURFACE DENSITY OF CHARGE (THE EQUIVALENT SURFACE) FOR MICACEOUS SILICATES)

| Mineral | Equiv. Surf. (Å²/unit chg.) | Degree of Swelling (Å) in Dist. Water, with Cations: | |
|---|---|---|---|
| | | $Na^+$ | $Ca^{2-}$ |
| Margarite | 12 | 0 | 0 |
| Muscovite | 24 | 1.9 | 2.8 |
| Celadonite | 27 | 2.4 | 2.8 |
| Sarospatak illite | 32 | 4.2 | 2.8 |
| Vermiculite (South Africa) | 36 | 5.1 | 4.3 |
| Beidellite I (Unterrupsroth) | 41 | 5.4 | 4.9 |
| Nontronite (Untergriesbach) | 46 | ∞ | 9.2 |
| Beidellite II (Unterrupsroth) | 57 | ∞ | 9.2 |
| Montmorillonite (Cyprus) | 60 | ∞ | 9.2 |
| Hectorite | 100 | ∞ | 10.6 |
| Pyrophyllite | ∞ | 0 | 0 |
| Talc | ∞ | 0 | 0 |

Summarized from Table 1 in Weiss (1958).

the First Congress (MacEwan, 1955). Since then, Weiss has assembled a mass of data bearing on the problem, and some of this is reproduced in Table 4.

This table shows that the swelling increases as the charge density decreases, but is also zero for zero charge. There ought therefore to be a particular value of charge density which gives maximum swelling, and on decrease of charge density beyond this point, the swelling ought to decrease. This, however, has never been observed. The trouble is, no doubt, that for very low values of the charge density, both the swelling force (due in large measure, probably, to solvation of the cations) and the attractive force (due perhaps to electrostatic interaction of the configuration charged sheet–cations–charged sheet) become very small.

Moreover, with swelling which is considerably greater than the maximum in Table 4 (disregarding the "∞" values), we probably pass into another

region of swelling characterized by different forces. This we have called (Ruiz Amil and MacEwan, 1957) "complete swelling," as opposed to "limited swelling."

This "complete swelling" was first investigated in detail by Norrish (1954). In Table 5, the two types of swelling are compared and contrasted. I have here introduced the term "Type 2 swelling" for the type investigated by Norrish, "Type 1" being the limited swelling. This seems better than "complete swelling," as the swelling is in fact always (or at least, often) limited, even in the "type 2" range. It will be seen from the table that a

TABLE 5.—THE TWO TYPES OF SWELLING SHOWN BY INTERLAMELLAR COMPLEXES

|  | Type 1 Swelling | Type 2 Swelling |
|---|---|---|
| Spacings | $< 60$ Å | $> 40$ Å (up to several hundred Å) |
| Type of complex | Single spacing with complete series of orders, or inter-stratification of a *limited* number of such single spacings | Spacings continuously variable within certain limits |
| Law of variation $d_{001}$ | Spacings depend on molecular orientation | Spacings vary as c |
| Interlamellar substance | Oriented layers of molecules | Normal liquid? |

clear distinction can be drawn, on several grounds, between the two types of swelling, although in terms of actual spacing values, their fields overlap. The large values of spacing with type 1 swelling are given by very long-chain molecules.

Type 1 swelling is the important type where studies of molecular orientation and bonding to the clay surface are involved. On the other hand, the type 2 swelling must be closely related to the general phenomenon of interaction between colloidal particles. It seems likely to permit considerable future development.


## THE MECHANISM OF INTERLAMELLAR SORPTION

Now I want to plead for another extension of the range of discourse, and this links up with the last two words of my title "other substances." We are really limiting our interests excessively if we confine ourselves to interlamellar sorption by clays alone. Exactly analogous phenomena are shown by other substances, and investigation of these substances may give valuable clues to the properties of clays.

Despite much experimentation and much thought on this problem, the mechanism of interlamellar sorption is not yet fully understood. One of the troubles is that such important features as charge density of the layer and the nature of the layer surface are not modifiable in natural materials. The use of artificial sorbents allows a wider range of variation.

One of the limitations of clays is that, with the exception perhaps of halloysite, they all have a negative charge on the layer. This is shown

TABLE 6.—SUBSTANCES SHOWING INTERLAMELLAR SORPTION

| Substance | Charge on Layer | Complexing Substances | Investigator(s) |
|---|---|---|---|
| (1) *Clay Minerals* | | | |
| Montmorillonite, etc. | — | Cations, neutral molecules | Numerous |
| Vermiculite | — | Cations, neutral molecules | Barshad, Walker, etc. |
| Halloysite | 0 or $\pm$ | Neutral molecules, salts | MacEwan; Henin, etc.; Walker |
| (2) *Other Minerals* | | | |
| Micas | — | Cations, neutral molecules (?) | Hofmann, etc. |
| U-micas, etc. | — | Cations, neutral molecules | Hofmann, etc. |
| Tobermorite etc. | ? | ? | |
| (3) *Chemical Precipitates, etc.* | | | |
| Graphitic acid | — | Cations, neutral molecules | Hofmann, etc.; MacEwan, etc. |
| Gypsum (ppt.) | ? | Neutral molecules (?) | Cano and MacEwan |
| Complex cyanides of $Fe^{3+}$, $Co^{3+}$, etc. | 0 | Neutral molecules | Weiss |
| a-hydroxides of $Zn^{2+}$, etc. | + | Anionic dyestuffs, neutral molecules | Talibudeen, etc. |

by Table 6, in which I have endeavored to make a list of substrates, together with an indication of the probable nature of the charge on the layer.

Among the artificial sorbents, $\alpha$-$Zn(OH)_2$ has a positive charge, and sorbs large anions in the same way as montmorillonite sorbs cations. The complex cyanides of transition metals occupy a special position in that the layers, according to Weiss, are neutral, and there are no interlamellar ions. If we are right about the influence of layer charge on interlamellar sorption, the mechanism here must be of a different nature, and Weiss considers the sorption to be conditioned by the tendency of the transition metal ions to surround themselves with a stable coordination shell of six molecules— four being in the layer and the other two being polar "heads" of sorbed molecules.

The case of halloysite is interesting. Garrett and Walker (1959) have shown that Rivière's (1948) attribution of a cation exchange capacity to halloysite is probably wrong, so that the layer probably has no net charge. However, clearly this is not the same case as that of cobalt cyanide. One side of the halloysite layer resembles the surface of montmorillonite, and should have a negative charge; the other resembles that of an α-hydroxide, which has a positive charge. We may therefore suggest that halloysite is an example of an amphoteric sorbent, having both positive and negative charges on opposite faces. It is probably of significance in this connection that, as Weiss, Mehler and Hofmann (1956), Garrett and Walker (1957, 1959) and K. Wada and M. L. Jackson (private communication, 1959) have shown, halloysite will form complexes with inorganic salts. The cyanides of transition metals have not been found to form such complexes.

Viewed from this angle, Rivière's (1948) determination of a fairly high cation exchange capacity for halloysite would be reconcilable with Garrett and Walker's (1959) rejection of such a result. Halloysite will in fact have both cation- and anion-change capacities, though these will only be determinable under suitable conditions for the entry of salt. As Garrett and Walker have shown, these conditions are quite restrictive.

## GRAPHITIC ACID AS AN ARTIFICIAL SORBENT

Graphitic acid is an example of a substrate which can be used to extend the available information on interlamellar sorption. Of course the validity of this statement depends on there being some real unity in the phenomena, *i.e.* on the supposition that the mechanism is essentially the same in graphitic acid and (say) montmorillonite. We believe there is substantial evidence that this is the case.

One of the advantages of graphitic acid is that it can be methylated in such a way as to affect the interlamellar surface. This is supposed to have been done with montmorillonite, but the evidence for a genuine interlamellar methylation has not been universally accepted. Methylation of graphitic acid profoundly affects its sorption properties, as has been shown by my collaborator, Mr. Aragon de la Cruz (1960).

The main features of these results which are summarized in Figs. 1, 2 and 3 can be explained by the decrease in electronegativity (acid character) of the layer as a result of methylation. The facility of formation of complexes with the basic amines decreases, there being a region of chain lengths (11–18 C atoms) where there is scarcely any increase of spacing with chain length for the methylated graphitic acid, whereas, with the unaltered graphitic acid, there is a steady spacing with chain length (Fig. 1).

On the other hand, the facility of complex formation with alcohols and fatty acids increases as a result of methylation. For the alcohols, the range

of existence of the β-complexes becomes greater (Fig. 2). For the fatty acids, no complexes at all are formed before methylation, but after methylation β-complexes are formed (Fig. 3).
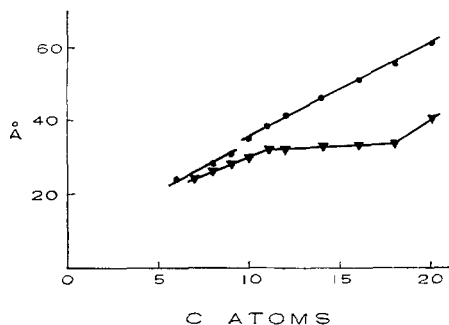


FIGURE 1.—$d(001)$ values for complexes of straight chain amines with graphitic acid. Circles, normal; triangles, methylated.
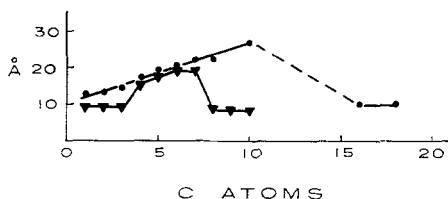


FIGURE 2.—$d(001)$ values for complexes of straight chain alcohols with graphitic acid. Circles, methylated; triangles, normal.
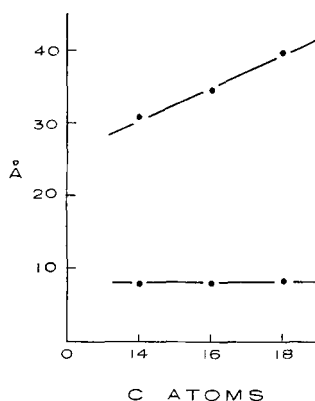
FIGURE 3.—$d(001)$ values for complexes of straight chain fatty acids with graphitic acid. Upper line, methylated; lower line, normal.

## POSSIBILITIES FOR FUTURE RESEARCH

Study of these complexes may make a considerable contribution to our understanding of colloidal phenomena, although the actual contribution which they have made must be admitted to be small to date. But the possibilities for experimentation in this field are almost endless. We can study the transition between complexes, in which the layers are separated by oriented layers of molecules, and macroscopically swollen material — gel or sol — in which the layers of sorbent are separated by typical liquid. This presents possibilities for shedding light on the nature of liquids, as well as

on the forces acting between colloidal particles. We can study the mixing and interaction of molecules in monolayers. We can study, using the beautifully simple technique described by Walker, the actual rate of migration of neutral molecules and ions in the interlamellar space. We can study the change in orientation of the sorbed molecules as their density on the sorbent surface is increased or decreased.

Some illustrations may be given from work recently done by Aragon (1960). Turning first of all to the question of mixed sorbates, Fig. 4 shows the variation in spacing of hexylamine–decylamine mixtures sorbed on graphitic acid (similar results probably would be obtained with montmorillonite). The jump on passing from 90 percent decylamine to pure decylamine may be ascribed to a phase change (solidification?) in the sorbed layer. A similar jump is found in the graph of spacing against chain length for the pure amines. Fig. 5 shows a similar diagram for mixtures of benzyl alcohol
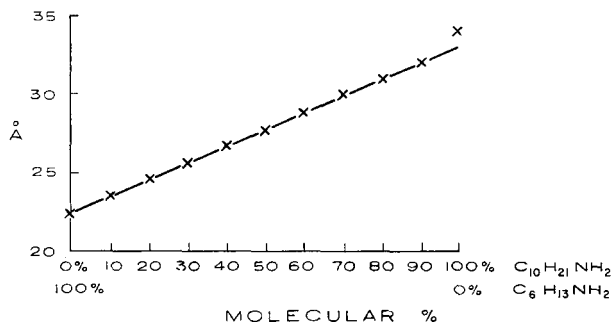


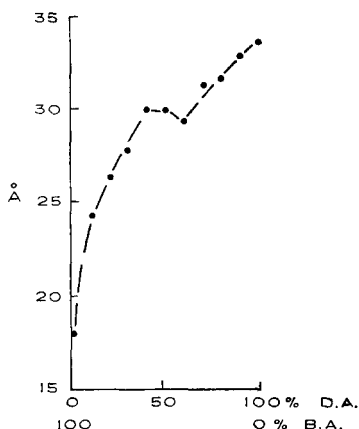FIGURE 4.—$d$(001) values for mixture of hexylamine and decylamine complexed with graphitic acid.



FIGURE 5.—$d$(001) values for mixtures of decylamine and benzyl alcohol complexed with graphitic acid.

with decylamine. Here the phenomena are more complex. There is a rapid rise in spacing on introducing the amine, followed by a stabilization of spacing which may correspond to an ordered structure, possibly opposed layers of alcohol and amine. Finally there is a linear region corresponding to progressive replacement of the alcohol layer by amine molecules. The "side-spacing line" characteristic of "solid" layers of sorbate (MacEwan and Aragon, 1959) appears in the region of the plateau (it may be significant that there is a decrease of basal spacing in this region (*i.e.* at about 50 percent decylamine), suggesting that a separation of the two types of molecule does in fact occur.

A further suggestion is that it may be possible to extend the applications of interlamellar complexes in identification. Hitherto we have used these complexes to identify the *minerals*, and progress is still being made in this field. But what about reversing the roles, and using the complexes to identify the organic components? This is a much vaster field, of course, but then, using both natural and artificial substrates, modified and unmodified, we have a great many possibilities of variation.

To take a rather specialized example, our own experience shows that the linear relationship between chain length and spacing for the normal amine complexes is good enough to enable quite small amounts of impurities (other amines, or completely unrelated substances) to be detected; or to enable the proportion of two different amines in a mixture to be determined quite accurately. For normal alcohols, a similar linear relationship obtains with methylated graphitic acid (Fig. 2). We have not yet checked the absolute linearity in this case.

Using the diffractometer, a determination of the spacing given by an interlamellar complex can be made in a very short time. By using various sorbents, at present available, a considerable amount of information about an unknown substance may thus be accumulated quite easily.

It should be noted that, for a chainlike molecule which is strongly sorbed — as amines on montmorillonite or graphic acid — by varying the proportion of sorbent and sorbate, a measure both of the length and width of the molecular chain may be obtained very rapidly. Aragon (1960) has shown, for example, that with (graphitic acid)–(decylamine) mixtures, as the amount of decylamine is reduced, the spacing decreases from the maximum of 34 Å — corresponding to fully extended chains—to about 25 Å; then on further decreasing the quantity, a sudden fall to about 10 Å takes place, the latter value corresponding to an $\alpha$-complex, and giving a measure of the thickness of the molecular chain. The reason for the jump is presumably that, for steric reasons (interference of neighboring chains), the inclination of the chains can only proceed up to a certain limit, after which the $\alpha$-complex arrangement is a better space-filler.

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