ORIENTATION AND PACKING OF ALIPHATIC CHAIN MOLECULES ON MONTMORILLONITE

Clay–Organic Studies—VI

by

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ABSTRACT
Aliphatic chain molecules may be adsorbed on montmorillonite surfaces with the zigzag of their carbon chain either parallel or perpendicular to the surface. These orientations are designated \( \alpha_\Pi \) and \( \alpha_1 \), respectively. Fourier syntheses have too few terms to distinguish clearly between these orientations. The problem is studied therefore by consideration of the basal spacings. These spacings are appreciably less than the sum of the van der Waals cross-section of the molecules plus the thickness of the montmorillonite layer. Chemical bonding or geometrical packing, or both, appear as possible explanations.

Previous studies have shown that CH activity influences the shape of the adsorption isotherms, but infrared studies of the adsorbed molecules have shown no appreciable change in the CH-stretching frequencies. This suggests the importance of the CH activity for organic–organic interaction on the clay surface rather than for clay–organic interaction itself.

The possibility of geometrical packing is studied by means of molecular models and it is shown that an appreciable contraction can occur at a clay–organic interface owing to a keying of the molecules into the surface structure. This is possible equally well for the \( \alpha_\Pi \) and the \( \alpha_1 \) orientations.

From the information available, it appears that the \( \alpha_\Pi \) arrangement is adopted by aliphatic chain molecules containing strongly polar groups in order to place the dipole parallel to the silicate surface, while the \( \alpha_1 \) arrangement is favored by other aliphatic chain molecules possibly because this provides a favorable organic–organic interaction.

INTRODUCTION
It has been known for many years that montmorillonite takes up organic molecules in its interlayer space by adsorption processes and by exchange reactions. Among the earlier investigations, the work of Gieseking (1939),

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Ensminger and Gieseking (1939, 1941), Hendricks (1941), Bradley (1945), and MacEwan (1948) may be specially mentioned.

Following MacEwan, the orientations can be placed in $\alpha$ and $\beta$ categories corresponding respectively with the plane or chain of the molecule lying parallel with or inclined to the silicate surface. In predominantly aliphatic compounds, the $\alpha$-complexes may be subdivided into $\alpha_{II}$, those with the zigzag of the carbon chain parallel to the silicate surface, and $\alpha_{I}$, those with the plane of the zigzag perpendicular to the surface.

Experience has shown that it is not easy to obtain a clear differentiation between $\alpha_{II}$ and $\alpha_{I}$ orientations for chain molecules, neither by the direct approach using Fourier synthesis, nor on the basis of X-ray lattice spacing data. The latter approach is handicapped by uncertainties introduced by an apparent shortening of contact distances between the organic molecules and the silicate surface. The nature of this shortening of contact distances needs to be discussed again in the light of new experiments.

Two basic questions will be considered:

1. What orientations are taken up by organic chain molecules in the interlayer space of montmorillonite?

2. What is the nature of the apparent shortening of contact distances between organic molecules and the silicate surface?

A review of the subject is presented together with additional data obtained by X-ray diffraction and by infrared absorption techniques.

**Orientation of Aliphatic Molecules Adsorbed on Montmorillonite**

It should be possible from X-ray data to determine the orientation of organic molecules in the interlayer space of montmorillonite by two methods: (i) by direct Fourier synthesis; (ii) via the lattice spacings and molecular dimensions of the organic molecules and the montmorillonite lattice.

**Information Provided by Fourier Syntheses**

One-dimensional Fourier syntheses based on the 001 reflections from a montmorillonite-organic complex would be expected to provide valuable evidence on the organization of the organic molecules in the interlayer space. Unfortunately the limitations imposed by the nature of the material preclude measurements of sufficiently high orders of reflection to give the required resolution.

Bradley (1945) gave Fourier "sketches" based on from six to nine orders of reflection (minimum spacing measured, $d_{min} \approx 1.8 \, \text{Å}$) and MacEwan (1948) obtained slightly higher resolution using reflections down to $d_{min} \approx 1.67 \, \text{Å}$. These analyses showed clearly that the organic material
was organized in layers, one, two, and occasionally three layers being observed, but the molecular orientations were not evident beyond the recognition that the axes of the chains lie parallel to the surface. Brown (1950) measured fourteen orders of reflection from a glycerol-saturated Tl-montmorillonite ($d_{\text{min}} \approx 1.3 \, \text{Å}$) but the detailed organization of the organic molecules still was not apparent.

Brindley (1956) using an ethylene glycol complex of the swelling mica-like mineral allevartite, obtained reflections as far as 00.22 corresponding to $d_{\text{min}} \approx 1.2 \, \text{Å}$ and the resulting Fourier synthesis pointed to an $\alpha_1$ arrangement of the organic molecules. Fig. 1 shows the Fourier synthesis obtained and the probable molecular arrangement between the silicate sheets. The more clearly defined results obtained with this mineral are almost certainly due to its superior crystallinity.
Since Fourier synthesis of montmorillonite complexes seldom can be carried out with sufficient resolution, it is important to examine critically the information which can be obtained from spacing measurements.

**Information Provided by Spacing Data**

Following MacEwan (1948), the difference $A$ between the expanded and unexpanded spacings of montmorillonite can be regarded, at least to a first approximation, as the space occupied by the organic molecules.

$$d(001, \text{expanded}) - d(001, \text{unexpanded}) = A$$

The value of $A$ increases in a stepwise manner as one, two, or three layers of organic molecules are accommodated in the interlayer space. It is simpler to consider mainly the one-layer complexes when studying the orientation problem because of the possibility of some kind of close packing between the molecules when two or more layers are present, for which there is no easy way of correcting the $A$-values. If the cross section of the adsorbed molecules is different in different directions, comparison with the observed $A$-values would allow the assignment of a certain orientation.

It was evident in the early studies that the $A$-values correspond approximately to the molecular dimensions, but when a detailed comparison was made many sources of uncertainty were found. However, Bradley (1945) considered the observed spacings to be generally smaller than would be expected from the known dimensions of the unexpanded mineral, and the van der Waals radii for the contacting atoms. MacEwan (1948) encountered similar problems and considered that aliphatic chain molecules must "lie as flat as possible," i.e., the $\alpha_{\text{II}}$ arrangement, to obtain agreement between observed and calculated $A$-values. Glaeser and Mering (1953) found the spacing of a cyclohexanone complex smaller than expected by assuming regular van der Waals radii.

The situation was reviewed by Greene-Kelly (1955, 1956), who concluded that a shortening of the contact distances occurs generally at a clay–organic interface such that for a one-layer complex (with two interfaces) there is a contraction of about 0.7–0.8 Å in the spacing of the clay–organic complex compared with what would be expected from the known dimensions and van der Waals radii of contacting atoms. A somewhat larger contraction of the order of 1 Å is obtained for more expanded complexes. It is evident that any detailed discussion of the orientation of adsorbed molecules on the basis of $A$-values must take into account the shortening of contact distances, together with any uncertainties there may be in the numerical data. Conversely the question of orientation may have to be considered before one can arrive at the amount of shortening of the contact distances. Thus in many (but not all) cases, these questions of orientation and of shortened contact distances are interconnected.
Conclusions regarding Orientation of Aliphatic Chain Molecules on Montmorillonite

Greene-Kelly (1955, 1956) concluded that aliphatic chain molecules tend to adopt the \( \alpha_I \) arrangement. His argument can be summarized as follows:

For saturated ring compounds such as piperidine hydrochloride the organic molecules (at least at low concentrations) lie parallel to the silicate surface. The molecule has a puckered or zigzag structure, and the plane of the zigzag is perpendicular to the silicate surface. In effect, this is an \( \alpha_I \) arrangement. It gives rise to a spacing of about 13.3 Å. Other measurements for the piperidine-montmorillonite complex have given spacings of about 13.5 Å.

On the other hand, unsaturated ring compounds such as pyridine hydrochloride give spacings of about 12.5 Å, and this smaller spacing is consistent with the flat form of the molecule. The difference between the two spacings, 0.8–1.0 Å, is what would be expected from the form of the molecules.

When these data are compared with those for straight chain amines, which have spacings of the order of 13.3–13.5 Å, it seems evident that the straight chain molecules must be oriented in the \( \alpha_I \) arrangement, i.e. with the zigzag plane perpendicular to the silicate sheet. Greene-Kelly concludes: “It is difficult to avoid the conclusion that the zigzag of chain molecules ... does not lie parallel to the \((001)\) planes.”

A similar conclusion has been reached by Hoffmann and Brindley (1960) from a study of sixteen aliphatic chain complexes. With alcohols and polyethylene glycols, one-layer complexes were obtained having spacings in the range 13.25–13.65 Å, and these data agree with those of Greene-Kelly for molecules in the \( \alpha_I \) orientation. A second group of compounds, mainly ketones and esters, was found to give lower spacings in the range 13.0–13.1 Å and these were considered to have the \( \alpha_{II} \) orientation, not only because of the smaller spacing but also because the polarity of the carbonyl and carboxyl groups probably orients the \( \mathrm{C} = \mathrm{O} \) bonds parallel to the negatively charged silicate sheets.

These conclusions were further substantiated by data for 2,4-hexadiynediol-1,6 (\( \text{HOCH}_2 \:- \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - \text{CH}_2 \text{OH} \)), a completely linear molecule, which gives rise to a 13.0 Å spacing, similar to those of the ketones. This molecule can form a complex only of the \( \alpha_{II} \) type.

It therefore can be concluded that aliphatic molecules with strongly polar groups prefer an \( \alpha_{II} \) arrangement, and those without such groups the \( \alpha_I \) arrangement.
THE SHORTENING OF CONTACT DISTANCES

The Reported Values

From the molecular dimensions and our observed layer spacings (Hoffmann and Brindley, 1960), a contraction of about 0.6–0.8 Å is calculated for the \( \alpha_1 \) complexes, and about 0.4–0.6 Å for the \( \alpha_{II} \) complexes. These data confirm the contraction of a one-layer complex by about 0.4–0.8 Å and also show that both the \( \alpha_{II} \) and the \( \alpha_1 \) arrangements of many aliphatic chain molecules are subject to this correction.

Other data can be cited which appear to be in general agreement with these findings. Talibudeen (1955) studied five complexes with amino acids and his data lead to an apparent shortening of about 1.1 Å. Greene-Kelly (1955) obtained 0.7–0.8 Å for one-layer complexes. Greenland (1956) examined five complexes with sugar molecules and he concluded that there was no shortening “in contrast to the findings of Greene-Kelly.” Greenland estimated the organic molecular dimensions by taking crystal structure data for the pyranose and furanose rings and then making the necessary adjustments for the chemical groups around the rings. The present writers have repeated the calculations of some of the molecular dimensions using Pauling’s radii and find a shortening of the layer spacings of about 0.4 Å.

Table 1 summarizes the data for the apparent contraction of the layer spacings as calculated from the dimensions of the silicate layer and of the organic molecules using the van der Waals radii given by Pauling (1960) for the atoms in contact at the silicate/organic interfaces.

<table>
<thead>
<tr>
<th>Source</th>
<th>Shortening</th>
<th>Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. Greene-Kelly (1955)</td>
<td>1.0 Å for ( d(001) &gt; 14 ) Å</td>
<td>Sixty-one aromatic complexes</td>
</tr>
<tr>
<td>O. Talibudeen (1955)</td>
<td>0.7–0.8 Å for ( d(001) &lt; 14 ) Å</td>
<td>Five complexes with amino-acids</td>
</tr>
<tr>
<td>R. Greene-Kelly (1956)</td>
<td>&gt; 1.0 Å</td>
<td>Five complexes with cycloaliphatic compounds</td>
</tr>
<tr>
<td>D. J. Greenland (1956)</td>
<td>no shortening</td>
<td>Five glucose complexes</td>
</tr>
<tr>
<td>Greenland’s data, rec. by present writers</td>
<td>0.4 Å</td>
<td>do</td>
</tr>
<tr>
<td>R. W. Hoffmann and G. W. Brindley (1960)</td>
<td>0.4–0.8 Å</td>
<td>Seventeen complexes with aliphatic compounds</td>
</tr>
</tbody>
</table>
Are the layer contractions real or can they be attributed to errors in the calculations?

Before considering the nature of the shortening of contact distances, it is essential to consider whether there is a real contraction, or if it is only apparent and produced by an accumulation of errors in the calculations.

In calculating \(\Delta\)-values, it is necessary to know the unexpanded spacing of the montmorillonite. A survey of the literature shows that the majority of investigators have used one of the following values: 9.4 Å, 9.5 Å or 9.6 Å. These values are obtained experimentally and also by calculation from the known structure. Only a small minority have used values outside this range.

The distances between oxygen ion planes in the montmorillonite or mica layer structure is close to 6.6 Å. For muscovite, Gattegno and Mering (1958) have made an accurate determination and found the value 6.62 Å. If the van der Waals radius of oxygen is 1.4 Å, as given by Pauling (1960), then the unexpanded layer thickness is 6.6 + 2(1.4) = 9.4 Å. The present authors have adopted the value 9.5 Å, which is an average of those previously used, and in comparing data from different sources (cf. Table 1) have based them on this value for unexpanded montmorillonite. The error in this value is probably not greater than 0.1 Å.

In calculating the dimensions of organic molecules, the uncertainties in bond distances and bond angles probably can be neglected in the present study. The van der Waals radii used are those given by Pauling (1960) and are considered to be "reliable only to 0.05 or 0.10 Å."

In the absence of any packing of the organic molecules into the silicate surface, or of chemical bonding of the molecules to the surface, the spacing of a clay-organic complex should be the combined spacing of the silicate layer plus the cross-section of the organic molecule, and the uncertainty should be no more than about 0.3 Å. There seems little doubt that the observed spacings are indeed smaller than the calculated values.

ORIGIN OF THE SHORTENING OF CONTACT DISTANCES

Two explanations can be brought forward for this effect, namely:
(i) chemical bonding of the adsorbed molecules to the silicate surface; and
(ii) geometrical packing of the adsorbed molecules into the silicate surface.

Chemical Bonding as the Cause of the Shortening

Chemical bonding, and especially hydrogen bonding, is frequently considered as the origin of the shortening of contact distances. In order to test whether there are functional groups favoring chemical bonding to clay surfaces, Hoffmann and Brindley (1960) studied the adsorption isotherms of neutral organic molecules dissolved in clay-water systems. The results have shown considerable differences in the extents to which different mole-
molecules are adsorbed. Factors favoring adsorption appear to be (i) C – H activity, (ii) chain length. A chain length exceeding five or six atoms appears to be necessary. The role of activated methylene groups was recognized by MacEwan (1948) and by MacEwan and Talibudeen (1949), and even earlier by Bradley (1945) who concluded that adsorbed molecules are held not so much by hydrogen bonding of the O–H⋯O type as by a kind of hydrogen bonding over the methylene groups, a C–H⋯O interaction. The new data by the present writers give added weight to these earlier concepts.

These results suggest the possibility that C–H⋯O interactions may be important in shortening the basal spacings of montmorillonite–organic complexes. Interaction of this kind would be expected to produce marked frequency shifts of the molecular vibrations involved, as is known for other types of hydrogen bonding. A detailed study was made by Tensmeyer, Hoffmann and Brindley (1960) of the infrared absorption spectra of two compounds that are adsorbed strongly on montmorillonite, namely 2,5,8-nonanetrione and 2,5-hexanediol, of which the formulae are as follows:

\[
\begin{align*}
&\text{O} &\text{O} &\text{O} \\
&\text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}_3 &\text{(2,5,8-nonanetrione)} \\
&\text{O} &\text{O} \\
&\text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}_3 &\text{(2,5-hexanediol)}.
\end{align*}
\]

Each CH\textsubscript{2} group is activated by an adjacent C=O group. Comparison of the absorption spectra of these molecules (a) in solution, (b) in the solid state (2,5,8-nonanetrione only), and (c) when adsorbed on montmorillonite, showed no evidence for changes in the C–H stretching frequencies as would have been expected if C–H⋯O interactions to the silicate surface were important.

The sharp absorption spectra of the one-layer clay–organic complexes point to well-ordered molecular arrangements. The close similarity of the spectra of adsorbed 2,5,8-nonanetrione and of solid, crystalline 2,5,8-nonanetrione suggests similar bonding in the two cases, i.e. an organic–organic interaction rather than an organic–clay interaction.

The combined evidence from the adsorption isotherms and from the infrared study suggests that the CH-activity is related not so much to clay–organic interaction as to interactions between the adsorbed organic molecules themselves.

The influence of chain length on the adsorption isotherms probably reflects the influence of van der Waals forces between the molecules and the clay surface, but presumably this influence is not so great as to modify the C–H stretching frequencies to an appreciable degree.

Thus it appears that the adsorption of the investigated ketones is of a physical rather than of a chemical nature.
Geometrical Packing as the Cause of Shortening of Contact Distances

Since chemical bonding seems unlikely as the cause of the shortening, a geometrical packing of the adsorbed molecules must be critically examined.

The question whether organic molecules generally, and aliphatic chain molecules in particular, have dimensions that are compatible with those of the silicate surface, can be studied by means of scale models of the organic molecules and of the silicate surface. Many of the simpler organic molecules, both aliphatic and aromatic, can be keyed into the silicate surface to an appreciable extent in a variety of ways. Oxygen atoms in the silicate surface are arranged in lines at intervals of about 2.60 Å (twice the radius of the oxygen ion) and the repeat distance of a carbon chain is about 2.50 Å. The geometrical relations are very favorable for packing aliphatic chains parallel to lines of oxygen atoms. If the chain takes up the αII orientation it can be close-packed to the extent of about 0.4 Å at each organic/silicate interface; for the αI orientation, the packing varies between about 0.35 and 0.5 Å per contact depending on whether a methylene groups “sits” astride an oxygen atom or “rides” in the hollow between two adjacent oxygen atoms. The aliphatic molecules retain a high degree of mobility along the three main lines of oxygen ions in the silicate surface. This is consistent with a result established indirectly (Hoffmann and Brindley, 1961; Part IV of the present sequence of clay–organic studies) that adsorbed ketones possess a high surface mobility.

For aromatic rings lying on the silicate surface, an appreciable contraction is obtained, of the order of 0.2–0.3 Å, depending on how the carbon ring is related to the six-fold oxygen ring. For cycloaliphatic compounds, the most favorable packing position is again over the six-fold oxygen ring; if each hydrogen atom is placed between two oxygens, a packing contraction of about 0.5 Å is obtained, but if each hydrogen is placed adjacent to one oxygen atom, a contraction of about 0.2 Å is obtained.

It appears that the incompatibility of organic and silicate dimensions has been overemphasized in the past, and that many organic molecules (probably the simpler and more symmetrical types) can be packed on a silicate surface in a manner which provides for a degree of close-packing ranging from about 0.25–0.5 Å at each clay–organic interface. In other words, there appears to be no difficulty in attributing the observed layer contractions to a geometrical effect, either wholly or in part. Perhaps the small contractions observed for adsorbed sugars (Greenland, 1956) is a reflection of a lower compatibility for these particular molecules.

Plate 1 illustrates the packing of a number of molecular groups on an oxygen surface with the atoms arranged as in montmorillonite.
Plate 1.—Photographs of models illustrating possible packing arrangements of organic groups and molecules on the oxygen surface of a montmorillonite layer. (a) Left: CH₂ group placed between two oxygen atoms. Right: CH₂ group astride an oxygen atom. (b) Left: CH₃ · (CH₂)₄ · CH₃ chain in α₁ orientation. Right: The same chain in α₂ orientation. (c) Left: C₆H₁₂ ring with hydrogen atoms between pairs of oxygen atoms. Right: C₆H₁₂ ring with hydrogen atoms adjacent to oxygen atoms. (d) C₆H₆ ring showing contact between π-electron cloud of carbon atoms and the oxygen surface.
PACKING OF ALIPHATIC CHAIN MOLECULES

DISCUSSION

Whereas the $\alpha_{II}$ orientation of aliphatic chain compounds would seem to be the most probable because it yields the smallest spacing, in fact only aliphatic compounds with strongly polar groups favor this arrangement for reasons already given. So far no explanation has been found why other molecules favor the $\alpha_I$ arrangement and it is of interest to consider possible explanations.

In the first place, is the $\alpha_I$ orientation related to a preferential geometrical packing? No strong evidence for this view can be found. Geometrical packing is almost equally effective with both orientations, and both provide to some extent for organic–organic interaction.

Secondly, Emerson (1957) has shown that the spacing of a methanol–montmorillonite complex can be explained by taking account of the directional character of the bonding orbitals in the oxygen atoms of the clay surface. This approach essentially combines chemical bonding with geometrical packing. However, no preference for the $\alpha_I$ orientation of aliphatic chains can be found as a result of a directional element in the CH...O interactions. In the case of small molecules such as methanol, however, Emerson's explanation appears reasonable.

In looking again at the infrared evidence for the 2,5,8-nonanetrione and 2,5-hexanedione complexes, one is tempted to draw the conclusion that organic–organic interaction may be the explanation for the $\alpha_I$ orientation. However, it must be remembered that these molecules, being ketones, take up the $\alpha_{II}$ orientation. Therefore in these cases it must be argued that, despite the organic–organic interaction, the polar group plays the dominant role. However, in those aliphatic molecules which do not have such polar groups, it is conceivable that the organic–organic interaction is responsible for the $\alpha_I$ orientation.

It is evident that further investigations, combining detailed X-ray and infrared study, are necessary for complete elucidation of these problems.

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