

COMPLEXES OF CA-MONTMORILLONITE WITH
PRIMARY MONOHYDRIC ALCOHOLS¹
(CLAY-ORGANIC STUDIES—VIII)

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ABSTRACT

Complexes are formed between Ca-montmorillonite and even numbered straight chain primary alcohols, C₂-C₁₈. Four series of basal spacings are recorded. One-layer complexes and two-layer complexes are obtained with the chain molecules parallel to the silicate surfaces. Two series of long-spacing complexes are obtained. One series, C₆-C₁₈, is obtained at temperatures above the alcohol melting points; a second series, C₁₂-C₁₈, is obtained at temperatures below the alcohol melting points. The transition from the one to the other is reversible for the C₁₂-C₁₈ complexes. Molecular orientations are derived consistent with the experimental data, and also with O—H · · · O bonding of the alcohol molecules to the silicate surface.

INTRODUCTION

Since primary monohydric alcohols are among the simplest organic compounds, it is important for any general understanding of clay-organic relations that the complexes they form with montmorillonite should be examined carefully. The data available at present come mainly from the work of MacEwan (1948), Barshad (1952) and Glaeser (1954) who collectively have studied the complexes formed by the primary alcohols C₁ to C₁₀, C₁₄ and C₁₆.²

Their results are in broad agreement and can be summarized as follows: Alcohols C₁ and C₂ form complexes with basal spacings of about 17 Å corresponding to two layers of organic molecules between the montmorillonite layers, but at less than full saturation single layer complexes occur with basal spacings around 12.8 and 13.2 Å respectively.

Alcohols C₃-C₁₆ (with the possible exception of C₉ and C₁₀) form single layer complexes with basal spacings around 13.5-14.5 Å, and double-layer complexes appear not to be formed. The orientation of the aliphatic chain molecules in relation to the silicate surface in these complexes, *i.e.*, whether the zig-zag of the molecules lies parallel or perpendicular to the surface, has been discussed and summarized by Greene-Kelly (1956), Emerson (1957) and Brindley and Hoffmann (1962), and for primary monohydric alcohols it seems most likely that the zig-zag plane of the molecule lies perpendicular to the surface.

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² It is convenient to refer to these alcohols in terms of the number of carbon atoms in the chain.

Exceptional results were reported by Barshad (1952) for complexes formed by the C₉ and C₁₀ alcohols, for which he obtained basal spacings of 34.4 and 36.8 Å respectively, corresponding to double layers of chain molecules standing more or less on end between the montmorillonite sheets. He considered these arrangements were related to certain critical values of the dielectric constant of the medium. These apparently anomalous results require further examination.

From the extensive studies of Jordan, of Hoffmann, Weiss and their colleagues, and of many other investigators (see surveys by Weiss, 1963 a, b) it is evident that aliphatic chain molecules frequently can take up orientations more or less normal to the silicate layers in addition to forming complexes in which these molecules lie parallel to the silicate layers. Weiss has studied complexes formed by n-alkylammonium montmorillonites with various n-alkyl liquids, including alcohols, and finds that when such complexes are fully saturated, the chain molecules stand normally to the silicate surfaces in double layers with the HO- and H₃N-terminations adjacent to the oxygen surfaces of the clay, but that with "slight grinding and simultaneous evaporation of the swelling liquid" the spacings are reduced by an amount corresponding to the chains being inclined at about 56° to the clay surface. In these complexes the alkylammonium cations probably play a major role and the behavior of the alcohol or other swelling liquid is probably secondary. Certainly the behavior of alcohol molecules in the presence of small inorganic cations such as Na and Ca cannot be inferred.

The results to be presented show that straight chain alcohol molecules, C₂-C₁₈, even numbers only, take up a variety of orientations depending on the chain length of the molecules and the temperature, and also on the conditions of preparation which determine the degree of saturation of the silicate surfaces with alcohol molecules. The investigation is concerned with those aspects of the problem which can be evaluated by x-ray diffraction measurements.

EXPERIMENTAL

X-ray measurements; basic materials. A calcium saturated montmorillonite from Black Hills, South Dakota, was used in most experiments. Preliminary results on a sodium saturated form of the same clay were less satisfactory and subsequent work was confined to the calcium form. X-ray measurements were made on thin oriented layers of the clay on glass slides, using a Philips diffractometer and filtered Cu-K α radiation. The angular opening of the radiation shield was covered with scotch tape and the center part of the shield drilled to take a $\frac{1}{4}$ -in. diameter tube which permitted dry air, heated or cooled as required, to be passed into the

sample chamber. The sample temperature was determined by an adjacent thermocouple. Small open trays containing organic liquids or P_2O_5 were placed, as desired, in the sample chamber.

Even-numbered alcohols from C_6 to C_{20} were obtained from the Continental Oil Company, New York, and were used in the as-supplied condition. They are stated to be around 95–98% pure. Alcohols C_6 – C_{10} are normally liquids which increase in viscosity with increasing chain length; alcohol C_{12} melts at $22^\circ C.$; alcohols C_{14} – C_{20} are waxy solids giving sharp x -ray powder diffraction patterns. No detailed attention was given to the x -ray data of the solid alcohols.

Preparation of clay-alcohol complexes. The clay samples, prepared as thin layers on glass slides, were dried in an oven at around $250^\circ C.$ for $\frac{3}{4}$ hr and stored over fresh P_2O_5 until required. Basal spacings of 9.7 \AA for the Ca-clay and 9.6 \AA for the Na-clay were obtained. Care was taken to exclude water from the clay in all subsequent handling and to avoid organic vapor contamination either directly or by use of the same P_2O_5 desiccator for more than one alcohol complex.

The formation of satisfactory complexes between the clay and most of the alcohols proved unexpectedly difficult and only in the case of the C_2 complex was a satisfactory product obtained simply by exposing the clay to the liquid or its vapor. Basal spacing measurements have little direct significance unless they correspond to a regular sequence of lattice planes giving integral orders of Bragg reflections, and this was taken as the criterion of a satisfactory complex. The number of reflections obtainable was about five or six at the most, and in less favorable cases, no more than three were measurable. The spacing data usually carry an uncertainty of the order of 1% in the average values, but with this degree of accuracy the main conclusions are clearly established.

Complexes with the C_4 and C_6 alcohols were obtained by using the C_2 complex as a starting material. A drop or two of the C_4 or C_6 alcohol was placed in contact with the C_2 -clay complex so that a thin layer of C_4 or C_6 spread over the clay surface. To make certain that the clay was still saturated with C_2 , though covered by the film of C_4 or C_6 , a tray of C_2 was placed in the sample chamber. X -ray data showed no change in the clay complex so long as C_2 was present in the atmosphere surrounding the sample. The tray of C_2 was then replaced quickly by one containing C_4 or C_6 . As the sample lost C_2 , possibly aided by a slow stream of dry air, it absorbed C_4 (or C_6) from the surface layer. It was found repeatedly that the C_4 and C_6 complexes were formed best from a fully expanded C_2 complex.

Pursuing the same method with C_8 and C_{10} alcohols gave very unsatisfactory results. A procedure was then followed of preparing a regular C_6

complex and using this as a base for preparing the C_8 and C_{10} complexes in much the same way as the C_4 and C_6 complexes were prepared from the C_2 complex, but the preparation appeared to be much more "temperamental." A stream of dry air through the sample chamber was used for removing the C_6 and substituting C_8 or C_{10} .

To prepare complexes with still higher alcohols, which normally are solid, two possibilities existed, namely (i) to introduce the alcohols at temperatures above their respective melting points, and (ii) to use solutions in a volatile solvent. An excess of solid alcohol is troublesome since it contributes its own diffraction pattern containing many reflections. Although the solid alcohol reflections are sharper than those of the clay complex and therefore are recognized easily, it was always desirable to minimize these unwanted reflections. Experiments using method (ii) with C_6 as a solvent finally gave fairly good complexes with C_{12} , C_{14} , C_{16} and C_{18} alcohols. Usually the C_6 -clay complex was solvated with a C_6 - C_n solution, ($n=12$ to 18), in a C_6 atmosphere overnight; the C_6 was then removed by passing a dry air stream through the sample chamber on the diffractometer.

Effect of temperature on the clay-organic complexes. In addition to forming saturated complexes between montmorillonite and each of the alcohols of the series, attention has been given also to the effects of temperature on the complexes. In the first place, samples were heated gently in a hot air stream simply to remove part of the organic component, and thus to convert an expanded complex into one having a single layer of organic molecules. Subsequently, when studying the complexes formed by the higher alcohols, C_{12} - C_{18} , it was thought desirable to remove the reflections from the excess crystalline alcohols by raising the temperature above their melting points.

As the work continued, it was seen that structural changes were taking place in the clay-alcohol complexes as the temperature was taken above and below the melting point of the pure alcohol. The effects were reversible and apparently not related to a loss of organic material, although as the process was repeated and organic material was lost from the sample, these complexes were destroyed.

RESULTS

Table 1 lists the results obtained under various experimental conditions. The data are divided into four groups according to the nature of the complexes formed:

Single layer complexes. These show the smallest observed spacings, ranging from 13.2 to 14.1 Å as the number of carbon atoms increases; for the lower alcohols, the results agree with previously published data by Mac-

TABLE 1. BASAL SPACINGS, IN Å, OF MONTMORILLONITE-ALCOHOL COMPLEXES

Carbon atoms in alcohol	Single-layer series	Double-layer series	Above M.P. series	Below M.P. series (Room Temperature)
2	13.2 ₄ ± 0.2 ₅	16.6 ₈ ± 0.1 ₀	—	—
4	13.6 ₅ ± 0.1 ₀	17.8 ₁ ± 0.1 ₀	—	—
6	13.5 ₅ ± 0.0 ₆	17.8 ₅ ± 0.1 ₀	26.5 ± 0.2	—
8	13.7 ₆ ± 0.0 ₅	—	28.6 ± 0.3	—
10	13.8 ₁ ± 0.0 ₅	—	31.1 ± 0.4	(34.2 ± 0.7) ¹
12	13.8 ₃ ± 0.0 ₅	—	34.7 ± 1.4	43.5 ± 1.5
14	13.8 ₆ ± 0.1 ₅	—	37.8 ± 0.8	48.9 ± 0.5
16	14.0 ₆ ± 0.1 ₅	—	41.2 ± 1.3	53.3 ± 1.2
18	14.0 ₆ ± 0.0 ₆	—	41.0 ± 0.7	58.6 ± 0.6

¹ Value taken at about 0–5° C.

Ewan (1948), Barshad (1952), and Glaeser (1954). These spacings were obtained after a clay-alcohol complex had received treatment to remove part of the initially sorbed alcohol. In the case of C₂, C₄ and C₆, it sufficed simply to maintain a stream of dry air through the sample chamber on the diffractometer, but with the higher alcohols, more especially those which are normally solids, a mild heat-treatment was used such as a stream of hot air or leaving the sample in an oven at 110° C. for several hours.

Two-layer complexes. For the C₂, C₄ and C₆ alcohols, complexes were obtained with spacings of 16.7, 17.8 and 17.9 Å respectively. On the basis of 9.7 Å as the spacing of fully-collapsed Ca-montmorillonite, these spacings correspond to expansions (Δ -values) of 7.0, 8.1 and 8.2 Å which are twice the corresponding values derived from the shorter spacings, 3.5, 4.0 and 3.9 Å respectively. The results are consistent with the generally held view that complexes with these spacings have two layers of organic molecules lying with their lengths parallel to the silicate surfaces.

It is possible that similar complexes are formed transiently by the higher alcohols, but for reasons given later it was never possible to obtain these complexes without others also being present.

Long-spacing complexes. Table 1 shows data for two series of long-spacing complexes. One of these was observed first with C₆ alcohol and eventually was traced through to C₁₈, but for alcohols which are normally solid it was necessary to raise the temperature above the melting point of the pure alcohol. This series will be called the "above-melting point," or "above-M.P. series."

The second series of long-spacing complexes is observed with alcohols C₁₂–C₁₈, when measurements are made at room-temperature, *i.e.*, below

the melting points. This series will be called the "below-M.P. series."

The spacing measurements for the two series are shown graphically in Fig. 1, and the slopes of the mean straight lines give incremental spacings of 1.57 Å per carbon atom in the molecular formula for the above-M.P. series, and 2.48 Å per carbon atom for the below-M.P. series.

The transition temperatures from the one to the other type of complex corresponds, to within 2-3° C., with the melting points of the pure alco-

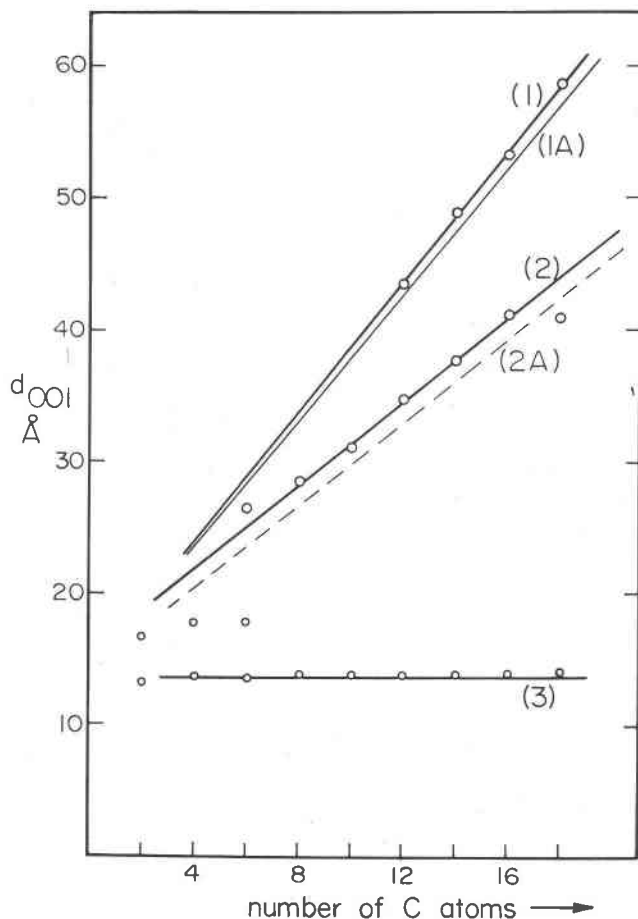


FIG. 1. Comparison of observed basal spacings (open circles) and calculated data (lines).

Line 1 : Model of Fig. 2(b), chain inclination 77°, equation (1).

Line 1A: Model of Fig. 2(b), chain inclination 70.5°, equation (1A)

Line 2 : Model of Fig. 2(c), ii; equation (2).

Line 2A: Model of Fig. 2(c), i.

Line 3 : Emerson (1957), model of Fig. 2(a).

hols. Since the alcohol C_{10} is normally a liquid and gives a complex of the above-M.P. type, an attempt was made to cool the complex below the melting point of the alcohol, $6^\circ C.$, in the hope of forming a complex of the below-M.P. type. As shown in Table 1, an expanded complex was obtained which, however, does not fall into line with the other below-M.P. complexes.

DISCUSSION

The most interesting result of these experiments is the discovery of two series of long-spacing complexes which form reversibly as the temperature is taken above or below the melting point of the pure alcohol. The general significance seems obvious, namely that the binding energy which holds the organic molecules in a regular array in the crystalline solid plays a similar role in the organic complexes.

The below-M.P. series of long-spacing complexes. The orientation of the alcohol molecules can be considered first in terms of the incremental spacing, 2.48 \AA per carbon atom of the molecular formula. The increase in length of an aliphatic chain per carbon atom is 1.27 \AA . The observed result can be explained only by a double layer of fully extended molecules standing almost perpendicular to the silicate surfaces. The angle of inclination of the chain length to the basal plane is $\sin^{-1}(2.48/2.54)$ which is 77° . This angle, being close to 90° cannot be determined with high accuracy but near perpendicularity of the molecular orientation is certainly established.

This type of arrangement in the below-M.P. series is broadly consistent with crystal structure data for the solid crystalline alcohols, which show fully extended chains parallel to each other, (see for example a recent study of $n-C_{16}H_{33}OH$ by Abrahamsson *et al.*, 1960).

Assuming this arrangement of the alcohol molecules, a calculation of the total spacing can be made using the following numerical data:

$O-H \cdots O = 2.60 \text{ \AA}$	radius of hydrogen, $r_H = 1.20 \text{ \AA}$
$C-C = 1.54 \text{ \AA}$	all bond angles = $109^\circ 28'$
$C-O = 1.43 \text{ \AA}$	chain inclination = 77°
$C-H = 1.08 \text{ \AA}$	silicate layer thickness = 6.60 \AA^1

With these values, and assuming that the $-CH_3$ terminations of the molecules make van der Waals contacts within the double layer, then the following equation is obtained:

$$d(001) = 19.16 + (n - 2)2.48 \quad (1)$$

where n is the number of carbon atoms in the molecule. The line corre-

¹ 6.60 \AA is the separation between centers of oxygen atoms on opposite sides of a montmorillonite layer. In the present calculations, the oxygen radii are taken into account in the length of the $O-H \cdots O$ bond. Similar calculations are set out fully by Emerson (1957).

sponding to equation (1) is shown in Fig. 1 and agrees *exactly* with the observed data.

An alternative way of regarding the molecular orientation follows from the model used by Emerson (1957) to explain the spacings of methanol montmorillonite, and of the one-layer complexes. He calculated these spacings on the supposition that the organic molecules are oriented by covalent-type bonds from the surface oxygens of the silicate layer to the hydroxyls of the alcohol molecules. In other words, the O—H · · · O bond is oriented at $54^{\circ} 44'$ to the normal to the silicate layer. Emerson's model is illustrated in Fig. 2(a). When the same method is applied to extended long-chain molecules (Fig. 2(b)) one readily calculates that the chain axis is inclined at 70.5° to the silicate surface which is close to the value of 77° derived above. On the basis of the model shown in Fig. 2(b), the following spacing equation is obtained:

$$d(001) = 18.62 + (n - 2)2.40 \quad (1A)$$

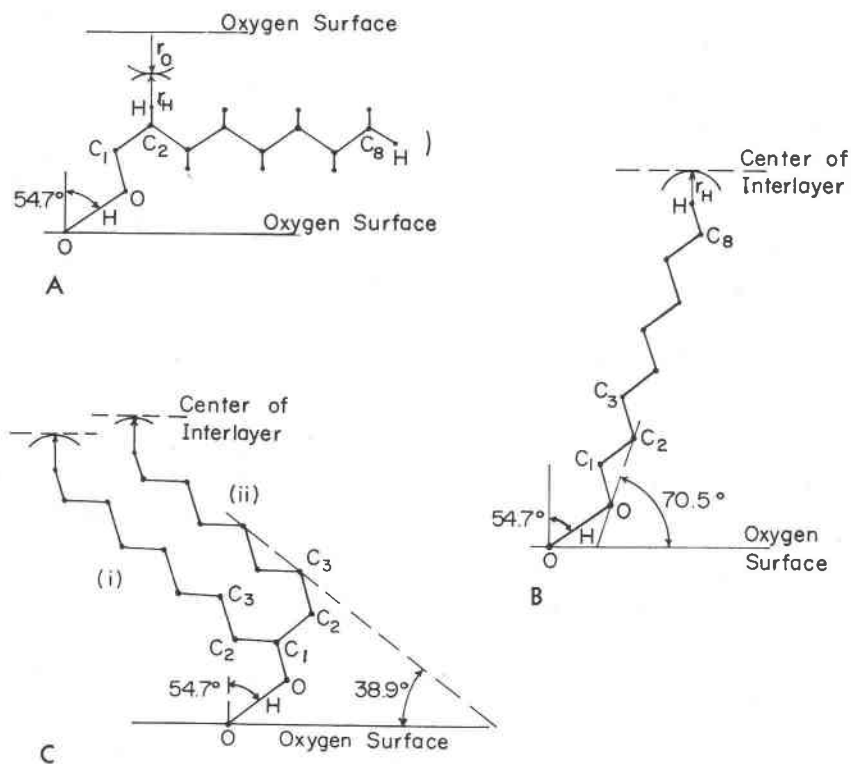


FIG. 2. (a) Emerson's model for one-layer alcohol-montmorillonite complexes. (b) Model for maximum spacing, alcohol-montmorillonite complexes (below melting-point series). (c) Possible models for alcohol-montmorillonite complexes (above melting-point series).

This relation also is shown in Fig. 1, and is labelled 1A.

The consistency of the results leads us to conclude that in the below-M.P. series, the chain molecules are fully extended, in double layers, and are inclined to the silicate surfaces at about 77° ; this angle is consistent with a covalent-type bond between the —OH groups and the surface oxygens.

The above-M.P. series of complexes. The measured incremental spacing of 1.57 \AA per carbon atom exceeds the *maximum* incremental spacing for a fully extended *single* layer of molecules, namely 1.27 \AA . This result together with the values for the total spacings shows that these complexes cannot be formed from single layers of molecules.

Possible arrangements of molecules in a double layer can be considered first in terms of the inclination of fully extended chains as derived from the incremental spacing. This angle is $\sin^{-1}(1.57/2.54) = 38^\circ$. Fully extended chains in double layers at this angle are not consistent with the type of $\text{O—H} \cdots \text{O}$ bonding previously described so that some less simple configuration seems probable, and doubtless there is more than one which may fit the experimental findings. However, a very simple solution is obtained by rotating a portion of the extended chain shown in Fig. 2(b) around the bond OC_1 or around C_2C_3 to give the configurations shown in Fig. 2(c). Arrangement (ii) in Fig. 2(c) satisfies all the requirements. The $\text{O—H} \cdots \text{O}$ bond is retained. The extended part of the chain makes an angle of 38.9° with the silicate surface which agrees with the angle calculated from the incremental spacing. Finally, the calculated spacing equation for this model is:

$$d(001) = 21.76 + (n - 4)1.58 \quad (2)$$

The corresponding line is shown in Fig. 1 and fits exactly the experimental values for the total spacings. Arrangement (i) in Fig. 2(c) gives total spacings which are slightly too small, (see dashed line in Fig. 1).

It is a relevant question to ask why, above the melting points of the crystalline alcohols, a molecular orientation of the type shown in Fig. 2(c) may occur, and below the melting points the straight chain arrangement shown in Fig. 2(b) seems to occur. It can be recalled that straight chain configurations exist in the crystalline alcohols and are stable because of the nature of the intermolecular forces. In the clay-alcohol complexes, the intermolecular forces cannot be exactly the same as in the crystalline alcohols but it seems likely that at the melting point of the crystalline compounds the thermal energy may be sufficient to loosen very considerably the intermolecular coherence in the clay-organic complexes. At the same time, the $\text{O—H} \cdots \text{O}$ bonds may remain stable; they seem to persist even in the one-layer complexes (Fig. 2(a)). There exists also the normal tendency for montmorillonite layers to collapse to a minimum

spacing owing to the ionic attractions between the silicate layers and the exchange cations.

Tentatively, it is considered that in the above-M.P. series the organic chains remain anchored by the O—H . . . O bonds but achieve greater mobility from the increased thermal energy and the breakdown of intermolecular bonds. They are also under compression from the ionic attractive forces. The resultant effect appears to be a bending of the molecules in the manner indicated in Fig. 2(c).

Although arrangement (ii) fits very well the available experimental data, other arrangements may be possible giving very similar (but not identical) spacings. This may be the reason for the absence of an extended series of Bragg reflections. The *x*-ray results point to some degree of inhomogeneity in the molecular spacings and this could arise from a variety of similar but not quite identical packing arrangements. The absence of clearly defined two-layer complexes for alcohols beyond C₆ also may be attributable to the same general cause. As the organic molecules bend and flatten, and also are gradually lost from the interlayer region, a homogeneous situation seems not to arise until the final stage is reached in which there is just a single layer of molecules arranged as in Fig. 2(a).

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