

COMPLEXES OF NATURAL AND SYNTHETIC  
Ca-MONTMORILLONITES WITH FATTY  
ACIDS (CLAY-ORGANIC STUDIES-IX)

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ABSTRACT

Short-spacing complexes ( $d(001) < 17 \text{ \AA}$ ) are formed with fatty acids up to and including C-9, and long-spacing complexes ( $d(001) > 20 \text{ \AA}$ ) with acids from C-10 to C-18. The latter exist only at temperatures above the melting points of the free acids. From the change of spacing  $d(001)$  with the number of carbon atoms, it appears that single layers of molecules standing at about  $65^\circ \pm 6^\circ$  to (001) are formed between the silicate sheets. If the molecules are attached equally to all silicate surfaces by active OH groups, packing considerations suggest a "head-to-tail" arrangement in pairs with some lengthwise displacement due to the bulky COOH terminations. The observed angle of tilt is shown to be consistent with a considerable degree of close-packing of the chain molecules among themselves, and also with possible close-packing between terminal OH groups and the silicate oxygen surfaces. Overall (001) spacings are consistent with van der Waals contacts and also with OH . . O bonds; the latter may be the cause of the preferred angle of tilt.

INTRODUCTION

The present investigation extends the work of Brindley and Ray (1964) on alcohol-montmorillonite complexes to another family of long-chain organic compounds, the fatty acids. Whereas the carbon chains of each family are essentially the same, the polar terminations are not, and a comparison of the alcohol and acid complexes may indicate the influence of the polar terminations. Parenthetically, it should be noted that these complexes may be involved in petroleum formation. Data given by Martin, Winters, and Williams (1963) suggest that the n-paraffins in petroleum are derived from fatty acids and Mair (1964) has provided additional data. Jurg and Eisma (1964) produced paraffins by sealing behenic acid and bentonite in a glass tube and heating. The present program differs from that of Weiss and his collaborators (see two summaries by Weiss, 1963a, b) who replaced the inorganic exchange ions of the silicate structures by alkyl ammonium ions, usually long chain molecules themselves. Being strongly sorbed by ionic forces and additionally by NH . . O bonds, these molecules will exert a powerful influence on the intercalation complexes formed by the alkylammonium silicates with other organic molecules. The present program, by retaining small inorganic exchange ions, permits the sorbed organic molecules to show more clearly their role in the resulting complexes.

## EXPERIMENTAL

*Layer silicates.* The layer silicates, both calcium saturated, were a natural Black Hills montmorillonite, and a synthetic fluormontmorillonite described by Johnson and Shell (1963), batch No. 25-211. The fluormontmorillonite with cation exchange capacity about 1.30 meq/g, gives  $x$ -ray diffraction patterns which are far better than, but otherwise identical with those of natural montmorillonites. Oriented films on glass slides were made from particles less than  $2\mu$  esd (equivalent spherical diameter) for the natural montmorillonite, and between  $20\mu$  and  $50\mu$  esd for the synthetic fluormontmorillonite.

*Organic compounds.* The saturated, unbranched fatty acids<sup>1</sup> employed were even numbers C-2 to C-20, and odd numbers C-9 to C-13. Fisher Scientific Company supplied C-2, C-4 and C-16 in reagent grade, Emery Industries, Incorporated, C-6, C-8 through C-14 and C-18 mainly 95% pure or better, and Eastman, C-20 in chemically pure grade. All chemicals were used in as-supplied purity. The  $x$ -ray diffraction patterns of the crystalline acids agreed with those in the literature.

*X-ray measurements.* The  $x$ -ray measurements were made with a Phillips diffractometer and filtered Cu-K $\alpha$  radiation. Scotch tape sealed the angular opening of the radiation shield, thereby creating a closed sample chamber. Dry air could be passed into the chamber through a hole drilled in the shield. The sample temperature, measured by an adjacent thermocouple, could be controlled by a hot or cold air stream. Trays containing organic liquids established the appropriate atmosphere in the chamber.

*Preparation of layer silicate-fatty acid complexes:* Water complexes often are very stable, and can interfere with forming montmorillonite (both natural and synthetic) complexes with organic compounds insoluble in water. Heating the oriented slides at 250° C. for  $\frac{3}{4}$  hour collapsed the basal spacing of both montmorillonites to about 9.7 Å, and hence removed most of the interlayer water. Water was excluded in all subsequent handling. The slides were stored in an oven at 110° C. until used.

By following different techniques, "short-spacing" or "long-spacing" complexes were made. The first type (with spacings less than about 17 Å) resulted from treating the dried montmorillonite directly with the fatty acid; the second type (with spacings greater than 20 Å) resulted from first "propping open" the dried montmorillonite with *n*-hexanol or *n*-octanol and then introducing the acid. The techniques are described in

<sup>1</sup> These acids are referred to conveniently by the number of carbon atoms in the chain.

detail because the complexes are *very* sensitive to the mode of formation, and negative results easily arise if great care is not exercised. Even so, their formation remains something of an art, and however carefully the various stages of preparation are defined, there appear to be other factors influencing the degree of success achieved. The presence of minute traces of water, either in the clay or in the organic materials may be such a factor.

Preparation procedures for the short-spacing complexes differed slightly for acids liquid or solid at room temperature. In the first case, a dried montmorillonite slide, in contact with a drop or two of the liquid acid, was stored overnight in a desiccator containing the acid, and then *x*-rayed at room temperature in an atmosphere of the acid. In the second case, a dehydrated montmorillonite slide, in contact with a small piece of the acid was placed in a closed jar containing the solid acid, which was kept in an oven at least 20°C above the acid melting point for two or more days. The slide was *x*-rayed at room temperature, and also about 10° C. above the acid melting point.

Forming the long-spacing complexes required greatly expanding the montmorillonite. A slide was taken directly from the 110° C. storage oven to the closed *x*-ray sample chamber, containing a tray of ethanol. Two or three drops of ethanol were added to the slide. Formation of a 16.6 Å ethanol complex was checked by *x*-ray diffraction. Then, one more drop of ethanol and two drops of n-hexanol were added to the slide, the tray of ethanol was replaced by one of n-hexanol, and a slow stream of dry air was blown through the chamber. The slide lost the ethanol, and adsorbed the n-hexanol, resulting in the formation of a 26.5 Å complex, which was checked by *x*-ray diffraction. About four drops of a fatty acid solution in n-hexanol (usually 25 weight per cent acid) were added to the slide, the n-hexanol tray was removed, and the dry air flow was continued. Ideally, as the dry air stream removed the hexanol, the montmorillonite adsorbed the acid, but with acids longer than C-12, only very poor, if any, long-spacing complexes formed, together with re-crystallized acid. However, when the slide was heated above the acid melting point by a hot air stream, the crystalline acid peaks disappeared, and the complex lines appeared. The complex was *x*-rayed about 20° C above the acid melting point.

In some cases, particularly with the longer chain acids which have low solubilities in n-hexanol, a n-octanol-montmorillonite complex was made from the n-hexanol complex by adding two drops of n-octanol to the slide, replacing the n-hexanol tray with one of n-octanol, and blowing dry air into the chamber. As the sample lost n-hexanol, the n-octanol was adsorbed, forming a 28.6 Å complex. A solution of the acid in n-octanol was added, and further procedure was the same as above.

Complexes could not be made merely by adding an acid-ethanol solution to the 16.6 Å ethanol-montmorillonite complex. However, a very weak complex was obtained by adding a C-10 acid-acetone solution to a 17.3 Å acetone-montmorillonite complex.

*Thermal degradation of complexes.* Certain complexes were heated in the diffractometer chamber up to 115° C. until all free acid had escaped. The presence of free acid was checked periodically by *x*-ray diffraction after cooling the slide below the acid melting point. Heating in the chamber continued until rapid changes had ceased. The slides were heated then for longer periods in a furnace at 110° C., 250° C., and 500° C. They were examined periodically by first being cooled in the furnace to about 110° C., and then being transferred to the diffractometer chamber, and *x*-rayed at room temperature in a dry air flow.

*Solvent degradation of complexes.* A C-10 acid fluormontmorillonite complex was covered with ethanol, and then carefully blotted with filter paper. After being treated three times, the slide was *x*-rayed in a dry air flow.

## RESULTS

Table 1 lists the observed basal spacings. The diffractometer patterns were graded on the basis of the sharpness and symmetry of the peaks, the number of measurable orders and the highest observed order, and the extent to which the pattern indicated an integral series of reflections. The basal spacings for the natural montmorillonite paralleled those for the synthetic material, but in all cases the latter appeared to be the more reliable. The highest observed orders did not go reliably to spacings lower than about 3 Å so that one-dimensional Fourier syntheses would have insufficient resolution to give useful results.

The experimental results are limited to basal spacing measurements and observations on the thermal and solvent stability of the complexes.

*Short-spacing complexes.* These were obtained with acids C-2 to C-9 but not with longer chain acids. Good short-spacing complexes were not obtained by heating long-spacing complexes. The observed spacings rather surprisingly do not approximate to constant values irrespective of chain length, nor do they show any simple trend with increasing number of carbon atoms.

*Long-spacing complexes.* These were formed only by using initially expanded montmorillonites, and with the acids C-10 to C-18. With acids

TABLE 1. BASAL SPACINGS,  $d(001)$ , OF FATTY ACID-MONTMORILLONITE COMPLEXES, IN Å, AT TEMPERATURES ABOVE THE FREE ACID MELTING POINTS

Acid	Natural montmorillonite complexes	Synthetic fluormontmorillonite complexes
C 2	16.5±0.1 (5) f	15.8 <sub>5</sub> ±0.1 (8) vg <sup>1</sup> 15.6 <sub>0</sub> ±0.1 (11) vg
C 4	14.1±0.1 (3) p	14.7 <sub>0</sub> ±0.1 <sub>5</sub> (7) g <sup>1</sup> 14.6 <sub>0</sub> ±0.2 (7) g
C 6	15.2 (1) p	15.0 <sub>5</sub> ±0.0 <sub>5</sub> (8) g <sup>1</sup> 14.9 <sub>0</sub> ±0.2 (7) g
C 8	14.4±0.1 (3) p	14.4 <sub>0</sub> ±0.9 (7) f
C 9	14.3±0.1 (3) p	13.1 <sub>5</sub> ±0.5 (7) f
C 10	29.2±0.2 <sub>5</sub> (2) p	29.9 <sub>5</sub> ±0.1 (11) g <sup>2</sup> 30.6 ±0.2 <sub>5</sub> (11) f <sup>2</sup> 30.6 <sub>5</sub> ±0.2 (11) g
C 11	31.2±1.4 (2) p	31.1 <sub>5</sub> ±0.0 <sub>5</sub> (11) f
C 12	32.2±0.7 (7) p	31.7 <sub>5</sub> ±0.1 <sub>5</sub> (11) f 31.9 <sub>5</sub> ±0.1 (11) f 31.8 ±0.2 <sub>5</sub> (11) g <sup>3</sup>
C 13	32.8±0.7 (3) p	32.6 <sub>5</sub> ±0.1 <sub>5</sub> (12) f
C 14	33.1±0.5 (3) p	34.6 <sub>5</sub> ±0.1 <sub>5</sub> (11) p 33.4 ±0.3 (10) p 34.2 <sub>5</sub> ±0.2 <sub>5</sub> (12) f <sup>3</sup>
C 16	36.7±0.2 (3) p	36.8 <sub>5</sub> ±0.1 <sub>5</sub> (13) f 36.6 <sub>5</sub> ±0.3 <sub>5</sub> (13) f
C 18	39.3±0.7 (4) p	40.5 <sub>5</sub> ±0.2 <sub>5</sub> (18) p 39.3 <sub>5</sub> ±0.3 <sub>5</sub> (18) p 38.6 ±0.2 (13) f <sup>3</sup>

<sup>1</sup> Obtained after a few hours contact only.

<sup>2</sup> Obtained about 3° C. below melting point of C 10 acid.

<sup>3</sup> Made via treatment with n-octanol—see text.

vg = very good; g = good; f = fair; p = poor; quality ratings of diffraction patterns—see text.

Numbers in parentheses indicate the highest orders observed.

C-8 and C-9 there was uncertainty whether the observed long spacings arose from the acid molecules or from difficulty in removing the n-hexanol or n-octanol used for the initial expansion. No success was obtained in attempts to form complexes with the C-20 acid.

The long-spacing complexes appear to be stable only at temperatures above the acid melting points. Many attempts to obtain results similar to those yielded by the alcohol-montmorillonite complexes, which gave two series of long-spacing complexes corresponding to temperatures respectively above and below the free organic melting points, were unsuccessful. A good C-10 fatty acid complex could be retained 3–4° C. below the acid melting point (31.5° C.), but 20° C. below it became very disordered. With the longer chain acids, it was found that as the temperature was increased, the free acid reflections disappeared sharply at the melting point and the reflections from the acid-clay complex at once appeared. On cooling and holding the temperature a few degrees below the acid melting point, the gradual decrease of the complex reflections and growth of the sharper acid reflections could be followed. The adjacent (001) reflections were particularly convenient for following these changes.

The reappearance of the free crystalline acid on cooling is not solely a recrystallization of excess liquid; acid molecules appear to be exsolved from the montmorillonite because as the free acid reflections grow in intensity, those of the montmorillonite complex become progressively weaker and disordered. The state of the montmorillonite below the acid melting point is not determinable easily because the diffraction pattern is dominated by the strong fatty acid reflections. However, when the pattern of the fatty acid on the montmorillonite is compared with that of the same fatty acid on an inert substrate, the difference between the two patterns indicates a poorly defined 16–17 Å spacing arising from a disordered fatty acid-montmorillonite complex.

*Thermal degradation by heat-treatment above the fatty acid melting points.* These results are a composite of the thermal behaviors of the complexes with C-10, C-11, C-13, C-14 and C-18 acids, but the trends are believed to be generally applicable. The long-spacing complexes formed above the fatty acid melting points continue to give mainly sharp reflections when held in a dry air stream up to 100° C. until the last of the free acid disappears (as shown by absence of acid reflections on cooling just below the melting point). Then the sharp complex lines are replaced by broad bands at slightly *higher* spacing. With heating for over 1 hr. the highest spacing band deteriorates while a very broad band at about 17 Å grows. Heating at 110° C. for up to 60 hr. reduces this spacing to about 14 Å. Heating at 250° C. for 70 hr. reduces it to about 13 Å. Heating at 500° C. for 40 hr.

finally collapses the fluormontmorillonite to about 9.6 Å, although the (001) reflection gives a slightly larger spacing than the average of other reflections which suggests that a small number of partially expanded layers may still persist.

*Solvent degradation.* The long spacing C-10 acid complex was reduced easily to a 13 Å complex by washing with ethanol. Inferences cannot be drawn from this short-spacing complex which may be contaminated with or even be mainly ethanol.

#### DERIVATION OF POSSIBLE MODELS FOR THE LONG-SPACING FATTY ACID-MONTMORILLONITE COMPLEXES

On the basis of the available experimental data and in the absence of adequately resolved Fourier syntheses, one cannot expect to derive a unique model for the arrangement of the fatty acid molecules between the silicate layers. Nevertheless it seems worthwhile to look into the questions involved even though the analysis in some respects becomes hypothetical.

*Chain inclination with respect to (001); the angle  $\phi$ .* When the long spacings,  $d(001)$ , are plotted against  $n$ , the number of carbon atoms in the fatty acid molecules, Figure 1, the results fall close to a straight line with  $\Delta d/\Delta(2n) = 2.278$  Å. This value can be compared with the increase in chain-length per two carbon atoms, about 2.52 Å–2.54 Å. If a *single* layer of fully extended chains is formed between consecutive silicate layers, and if the molecular configuration remains the same when the number of carbon atoms increases from 10 to 18, the chain inclination  $\phi$  is  $\sin^{-1}(2.278/2.52)$ , or about 65°. Any marked variation in  $\phi$  as the chain length increases would be shown by a non-linear variation of  $d(001)$  with  $n$ . If a *double* layer of fully extended chains is formed between consecutive silicate layers and the molecular configurations remains constant, then  $\phi$  becomes  $\sin^{-1}(2.278/5.04)$  or about 27°. No models could be devised to justify so small a value of  $\phi$  and the subsequent discussion will be based on a value  $\phi \simeq 65^\circ$ , the accuracy of which, however, needs to be considered. Since the sine of an angle changes rather slowly with angle beyond about 60°, the value of  $\phi$  is sensitive to the precise manner in which the mean experimental line is drawn in Fig. 1, and for a 5% variation in  $\Delta d/\Delta n$ , the angle  $\phi$  changes from about 60° to 72°. The chain inclination cannot be known more precisely from the available data.

For the alcohol-montmorillonite complexes (Brindley and Ray, 1964), (more particularly for the below-melting point series), an experimental value of  $\phi$  of about 77° was derived, which with an uncertainty of about

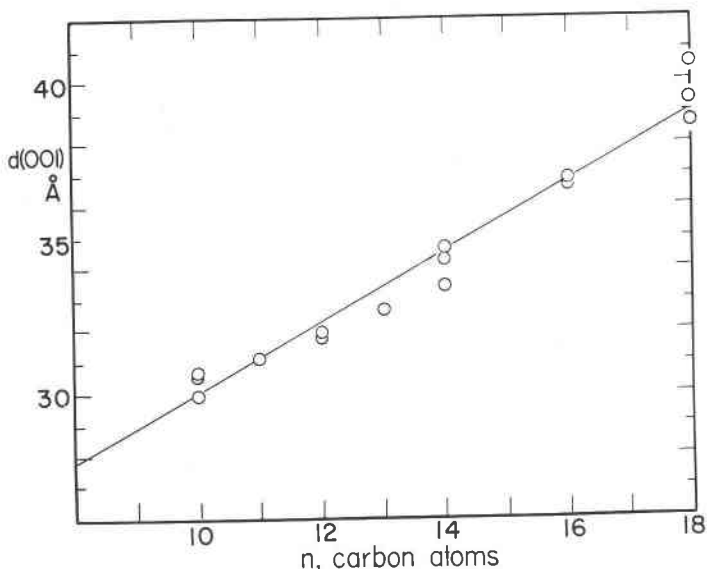


FIG. 1.  $d(001)$ , in Å, of fatty acid-montmorillonite complexes, against number of carbon atoms,  $n$ , in the fatty acid molecules. The data for the fluormontmorillonite are shown.

$\pm 5^\circ$  is not greatly different from the present value. Similar bonding conditions may be involved in both series of complexes. However, the alcohol complexes contained *two* layers of extended chain molecules between consecutive silicate sheets, whereas the fatty acid complexes appear to form only *single* layers of chain molecules.

*The overall basal spacings.* To explain the observed basal spacings, it is useful to construct a model based on the available information. By taking the overall spacing for any one complex, the known configuration of the fully extended chain molecule and its inclination  $\phi \approx 65^\circ$ , together with the known structure of the silicate layers, one finds at once that even the fully extended molecule is not long enough 'to bridge the gap' between adjacent silicate surfaces and falls short by an amount 3–6 Å depending on how the molecule is placed with respect to the surface. The discrepancy is least if a van der Waals contact is assumed, but if any "keying" of the molecule into the surface is considered and especially if OH...O bonding is assumed such as Brindley and Ray (1964) suggested for alcohol-montmorillonite complexes, then the discrepancy becomes greater.

*Chain packing arrangements.* If the molecules are attached in equal numbers and in the same manner to adjacent surfaces, they can be visualized



as extending in opposite directions across the intersilicate space, with the active  $-\text{COOH}$  terminations closely associated with the silicate surfaces and the inactive  $-\text{CH}_3$  terminations much less closely associated, or not associated, with these surfaces. This leads to a consideration of "head-to-tail" arrangements of the molecules in which the bulky  $-\text{COOH}$  groups are likely to play an important part.

The geometrical problems involved can be considered along lines suggested by the analysis given by Kitaigorodskii (1955) in which he separates considerations of chain packing from the various possible orientations of terminal planes. Figure 2 illustrates a model in which chain molecules are packed "head-to-tail" in pairs. A and A', B and B', etc., and all pairs being identical. Within a pair, A' can be displaced relative to A by  $\Delta L_1 = n_1c$  in the upward (*i.e.*, positive) direction, and pairs can be displaced relative to each other, for example B with respect to A, by displace-

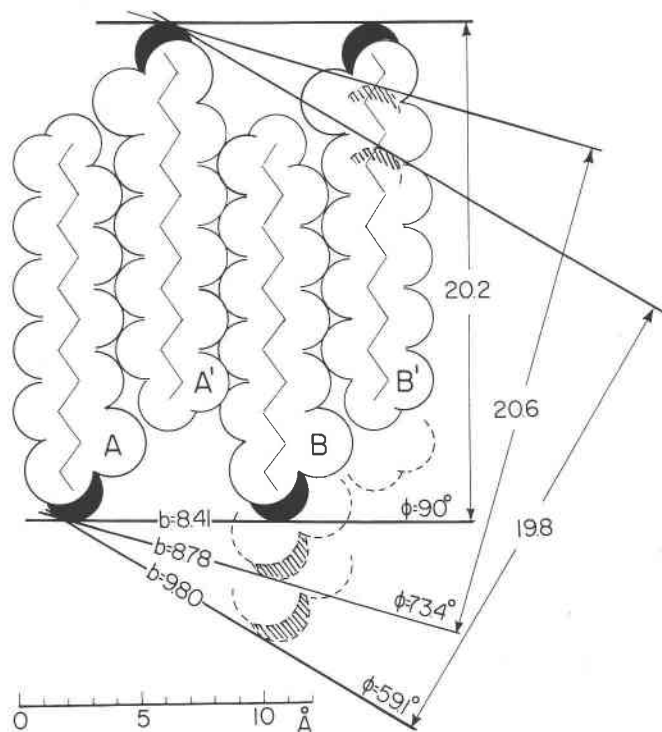


FIG. 2. Close packing of fatty acid molecules in pairs with head-to-tail arrangement. Dashed lines show various displacements of the pair B,B' with respect to A,A'. Spacings of terminal planes are shown and the corresponding angles of inclination  $\phi$  of chain axes with respect to the terminal planes. H's in terminal OH ions shaded.

ments  $\Delta L_2 = \pm n_2 c$ ;  $c$  is the chain periodicity, approximately  $2.52 \text{ \AA}$ . For each set of displacements characterized by  $n_1$  and  $n_2$ , the thickness of the organic layer measured perpendicular to the terminal planes touching the extreme OH groups can be calculated. The lateral packing of the chains shown in Fig. 2 assumes that a  $\text{CH}_2$  group of one chain lies between two such groups of a neighbouring chain, with the H atoms making van der Waals contacts. Successive chains are co-planar. Slightly closer packing is possible by off-setting alternate chains, so that an H atom of one chain

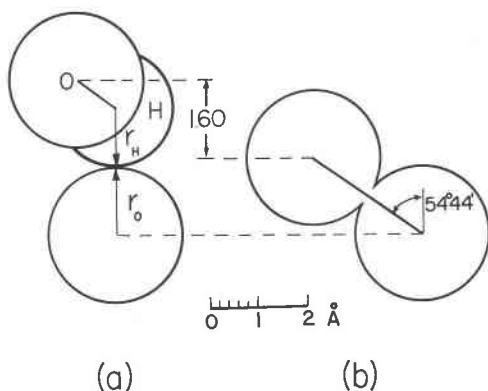


FIG. 3. A comparison of two spatial arrangements of the terminal OH group of a fatty acid molecule and a silicate oxygen atom. (a) shows a van der Waals contact, (b) shows two oxygen atoms of an  $\text{OH} \cdots \text{O}$  bonded pair.

touches four H atoms of the adjacent chain; such an arrangement is illustrated in Figure 4a. However, in this second arrangement hydrogen-carbon contacts may prevent the chains from coming appreciably closer in the projection shown in Fig. 2.

Figure 2 illustrates various arrangement of the chain molecules with respect to the terminal planes, and in this two-dimensional diagram, the angle of tilt  $\phi$  depends on the displacement  $\Delta L_2 = \pm n_2 c$ . Other displacements,  $\Delta L_3 = \pm n_3 c$ , can arise in moving in the third dimension normal to the plane of the diagram. The tilt angles illustrated in Fig. 2 can be labelled  $\phi_b$  to indicate that they arise from chain displacements as one moves in the  $b$  direction, left to right across the figure. Similarly one envisages  $\phi_a$  angles, and  $\phi_{a,b}$  angles. The present discussion will be limited to angles  $\phi_b$ .

To calculate overall spacings for the silicate-organic complexes, one needs to know additionally the nature of the silicate-organic contact. If no simple relation exists between the silicate parameters,  $a \approx 5.2$ ,  $b \approx 8.95 \text{ \AA}$ , and the organic packing parameters, then the van der Waals

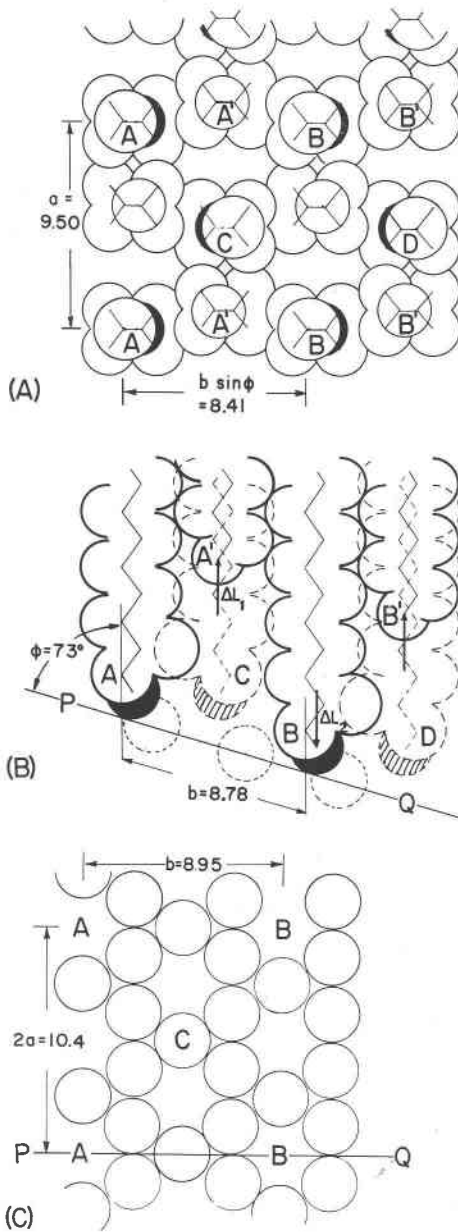


FIG. 4. An example to illustrate that a largely close-packed system of chain molecules, shown in (A) and (B), can have parameters  $a$  and  $b$  approximating to those of the silicate layer structure shown schematically in (C).

thickness of the silicate layer (about 9.40 Å) should be added to the thickness of the organic layer. If, however, OH . . O bonds are formed of the kind previously discussed (Brindley and Ray, 1964), then a correction term (Fig. 3) is required which reduces the overall spacing by about 3.2 Å. This situation can arise only when the OH bond in the organic molecule is directed towards a silicate oxygen at the appropriate "tetrahedral" angle and it requires a chain tilt of about 70°. A shortening of spacings due to geometrical "keying" of the OH-terminal groups into the hexagonal network of silicate oxygens cannot be precisely calculated but probably will not reduce overall spacings by more than 2 Å.

The calculated spacings<sup>1</sup> for the C-10 acid-montmorillonite complex based on various values of  $\Delta L_1 = n_1c$  and  $\Delta L_2 = \pm n_2c$ , and with either van

TABLE 2. CALCULATED SPACINGS,  $d(001)$ , IN Å, FOR C 10-MONTMORILLONITE COMPLEXES FOR VARIOUS MODELS INDICATED BY  $\Delta L_1$  AND  $\Delta L_2$ , AND FOR (a) VAN DER WAALS CONTACTS, AND (b) OH . . O BONDING, IN THE THIRD COLUMN,  $b$  IS THE ORGANIC PACKING PARAMETER

$\Delta L_2$	$\phi_b$ (degrees)	$b$ Å	d(001), with v.d. Waals contacts			d(001), with OH . . O bonds		
			$\Delta L_1=0$	$\Delta L_1=c$	$\Delta L_1=2c$	$\Delta L_1=0$	$\Delta L_1=c$	$\Delta L_1=2c$
-4c	39.9	13.10	26.43	28.04	29.65	—	—	—
-3c	48.1	11.30	27.83	29.70	31.57	—	—	—
-2c	59.1	9.80	29.20	31.36	33.52	26.00	28.16	30.32
-c	73.4	8.78	30.02	32.43	34.84	26.82	29.23	31.64
0	90.0	8.41	29.58	32.10	34.62	26.38	28.90	31.42
+c	106.6	8.78	26.62	28.03	30.44	—	—	—
+2c	120.9	9.80	24.88	27.04	29.20	—	—	—

der Waals contacts, or OH . . O bonding, are set out in Table 2. These values can be compared with the experimental value which lies in the range 30.0–30.6 Å, with the lower value 30.0 Å probably being the more nearly correct as judged from the mean straight line in Fig. 1.

From amongst the various models giving calculated spacings of about 30.0 Å, the following may be considered as being the more likely to occur:

(a)  $\Delta L_1 = 0$ ;  $\Delta L_2 = -c$ ;  $\phi_b = 73.4^\circ$ ; *van der Waals contacts*.

With  $\Delta L_1 = 0$ , each pair of chains (*c.f.* A and A' in Fig. 2) is packed as closely as the bulky C=O groups permit. With  $\Delta L_2 = -c$  (*c.f.* the dashed configuration of B and B' in Fig. 2) there remains considerable 'overlap' (*c.f.* A' and B in Fig. 2) between adjacent pairs. The angle  $\phi_b = 73.4^\circ$  agrees reasonably with  $65^\circ \pm 6^\circ$  determined from  $\Delta d/\Delta n$  in Fig. 1. If the contacts are of van der Waals type, consideration need not be given to particular packing arrangements on the silicate surfaces. Only in one

<sup>1</sup> The following interatomic distances in Å and angles are used; C-C 1.54, C-H 1.10, C-O 1.43, O-H 0.97, OH . . O 2.70,  $r_h = 1.20$ ,  $r_o = 1.40$ , all bond angles  $109^\circ 28'$ .

respect is the model inadequate; it provides no obvious explanation for the angle of tilt; one asks why  $\Delta L_2$  should not be zero and  $\phi = 90^\circ$  since this would give a maximum packing of the chains.

(b)  $\Delta L_1 = c$ ;  $\Delta L_2 = -c$ ;  $\phi_b = 73.4^\circ$ ; OH . . O bonding

(c)  $\Delta L_1 = 2c$ ;  $\Delta L_2 = -2c$ ;  $\phi_b = 59.1^\circ$ ; OH . . O bonding

Of these models, (c) gives a more acceptable spacing (30.3 Å) than does (b), (29.2 Å), and the tilt  $59^\circ$  given by (c) is nearer the experimental value than is  $73^\circ$  given by (b). However, model (b) is preferable to (c) in other respects. The smaller chain displacements of model (b) are preferable since they give a more compact arrangement. The angle  $\phi = 73^\circ$  is close to the ideal value,  $70^\circ$ , required for OH . . O bonding and this type of bonding offers an explanation for the chains being tilted at about  $70^\circ$ . If bonding of this kind is to occur any more frequently than would arise from chance coincidences of OH and O atoms, there must be an appropriate geometrical relation between the organic and the inorganic layer parameters. Table 2 shows that with  $\phi_b = 73.4^\circ$ , the  $b$  parameter of the organic layer is 8.78 Å (see Figure 2) which is strikingly near to  $b = 8.95$  Å for the silicate layer.

*A possible distribution of organic chain molecules to coincide with the silicate surface.* Such a distribution based on the preceding model (b) is illustrated in Fig. 4. Figure 4a shows the fatty acid molecules arranged in close-packed sequence in the  $b$ -direction and in close-packed pairs in the  $a$ -direction with alternate chains pointing in opposite directions with respect to the chain axes. The directions of the chain molecules are indicated by showing their lower terminations, OH or H. Figure 4b shows a projection looking along the  $a$ -direction, and the chains labelled A, A', B, B', C and D in Figure 4a are indicated also in 4b. Heavy arrows indicate the displacement  $\Delta L_1 = +c$  and  $\Delta L_2 = -c$ . The angle  $\phi_b$  is  $73^\circ$ , and the repeat distance  $b = 8.78$  Å for the organic layer is marked. Figure 4a shows that the chain distribution has an  $a$ -parameter of about 9.5 Å which comes close to  $2a = 2 \times 5.2 = 10.4$  Å for the silicate layer. Figure 4c shows the idealized hexagonal arrangement of oxygen atoms in the silicate structure. With a few per cent expansion of the organic pattern, there could be a good fit between the organic and inorganic structures.

It is not evident exactly how the OH terminations approach O atoms in the hexagonal rings and, for this reason, the possible sites of the chain terminations, A, B, C, D, on the silicate surface are indicated in Figure 4c only by the letters. If chains marked A and B coincide with holes in the oxygen arrangement, those marked C and D will fall above oxygen atoms. However, there need be no clash between chains C and D and oxygen atoms as can be seen from Fig. 4b.

It is *not* claimed that this model is the *only* way by which the chain

molecules can have a considerable degree of close-packing among themselves and also with respect to the silicate surface. However, it demonstrates the geometrical feasibility of such a situation.

#### DISCUSSION

*The short-spacing complexes.* Very few remarks can be made at present regarding these complexes. It is unusual that they show no obvious trend as the length of the molecule increases. At present, they cannot be interpreted with any confidence in terms of single layers or double layers of organic molecules lying flat on the silicate surface.

*The long-spacing complexes.* Since the various models previously described involve details which the available experimental data cannot confirm, a summary of the arguments supporting the favored hypotheses will be useful.

The measured incremental spacing  $\Delta d/\Delta n$ , obtained from Fig. 1, leaves little doubt that the organic molecules are arranged in single layers between the silicate sheets, with the chains standing at about  $65 \pm 6^\circ$  to (001). A plausible arrangement of the molecules in each layer distributes the active terminations, the  $-\text{OH}$  groups, equally over all the silicate surfaces. This leads to the concept of a "head-to-tail" arrangement which can account for the overall observed spacings in various ways. Perhaps this is as far as one can proceed justifiably on the basis of the experimental results.

In the more detailed analysis, it is shown that if the chains are stacked at an angle of  $\phi = 73^\circ$  to (001), adjacent chains fit together. Depending on how the oppositely directed molecules within a pair are displaced with respect to one another (the distance designated  $\Delta L_1$ ), the contact between OH groups and the silicate surfaces can be either of the van der Waals type (with  $\Delta L_1 = 0$ ) or a directed OH . . O bond (with  $\Delta L_1 = c$ ), and indeed both may occur. Also with  $\phi = 73^\circ$  the organic molecules can be matched more or less closely to the oxygen atoms in the silicate surfaces. The preference for a stacking angle of about  $73^\circ$  is seen therefore as a consequence of the favorable structural relations which it facilitates, including packing of the molecules among themselves, their distribution with respect to the silicate structure, and an orientation consistent with OH . . O bonds. Although the angle  $73^\circ$  differs somewhat from the experimentally determined value of  $65 \pm 6^\circ$ , the latter is not critical and a tilt of about  $70^\circ$  would satisfy all considerations.

*Stability of the long-spacing complexes.* Remarkably, these complexes are most stable *above* the melting point of the crystalline fatty acids, but not

*below*. This is consistent with the idea that some molecules are hydrogen bonded to the silicate surface whereas others are held more weakly. It can be proposed that the molecules which become hydrogen bonded enter the interlayer region when the alcohol molecules are holding the structure open, but sufficient acid molecules are not present to maintain the expansion upon departure of the alcohol. However, when the excess free acid melts, more molecules become available, and are adsorbed through mass attraction. The organic layer, attempting to achieve some degree of close-packing, expands. The particular orientation of the chains may be determined by the hydrogen bonds of some of the molecules to the silicate surface. For some reason, below the melting point, the weakly adsorbed molecules are more stable in the free acid crystal structure, and exsolve.

Interestingly, the thermal behavior of the molecules in the complex differs from that of the molecules in monolayers of fatty acids (Menter and Tabor, 1951); the monolayers become disorganized at temperatures *above* the melting points of the free acid, whereas the opposite holds for the fatty acid-montmorillonite complexes.

The ease with which the long-spacing collapses with solvent washing also supports the idea that many molecules are only weakly adsorbed.

The persistence of at least some expansion even after fairly rigorous heating is noteworthy and indicates that some of the organic material is very tightly held. Partial neutralization of the Ca exchange ions by the acid, and formation of an internal soap is a possible explanation.

*Comparison of fatty acid and alcohol complexes.* In comparing the fatty acid-montmorillonite complexes with alcohol-montmorillonite complexes, the importance of the polar terminations is evident. The fatty acids form stable complexes only above the melting point of the acid whereas the alcohols form two series of complexes, one stable above the alcohol melting point, the other series stable below. The structure of the acid and the alcohol complexes appear to be considerably different, but in both cases hydrogen bonding may be important. Full understanding of these complexes will require careful and systematic studies of other series of alkyl compounds.

*Comparison with the Results of Armin Weiss (1963).* Weiss (1963a, p. 205) also has noted that the basal spacings of particular complexes appear to vary with pre-treatment of the silicate host, though exactly reproducible results are obtained with standardized methods of preparation. In the present work, the observed spacings seemed to be very sensitive to pre-treatment, including even the prior aging of the Ca-montmorillonite.

Weiss (1963a, p. 197) records that in alkyl ammonium silicates, after saturation with alcohols, amines, aldehydes, or carboxylic acids, the chain molecules occupy a basal area of about  $21 \text{ \AA}^2$  per molecule. The model illustrated in Fig. 4 allocated 2 chain molecules per silicate cell of  $9.0 \times 5.2 \text{ \AA}^2$  area, or  $23 \text{ \AA}^2$  per molecule; the model is consistent with Weiss's data. The absence of any "even-odd" alteration in Fig. 1, showing spacing versus number of carbon atoms, calls for comment since Weiss (1963a, p. 209) found a marked alternation between even and odd numbered chains. Probably no such effect is observed in the fatty acid-montmorillonite complexes because the  $-\text{CH}_3$  terminations appear not to come into direct contact with the silicate oxygen surfaces.

#### ACKNOWLEDGMENTS

Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Thanks are tendered also to Dr. R. C. Johnson, Bureau of Mines, Norris Research Laboratory, Norris, Tennessee, for the preparation of the synthetic fluormont-morillonite, and to Dr. K. T. Mecklenberg and Emery Industries, Inc., Cincinnati, for many of the fatty acids used in these studies.

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*Manuscript received, February 5, 1965; accepted for publication, May 20, 1965.*