

# INTERLAMELLAR REACTIONS OF TETRACALCIUM ALUMINATE HYDRATES WITH WATER AND ORGANIC COMPOUNDS

*by*

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## ABSTRACT

TETRACALCIUM aluminate hydrates are the first example of layer-structured crystals containing neutral sheets, which are highly capable of interlamellar adsorption of water and neutral organic compounds. In this respect tetracalcium aluminate hydrates present new aspects of the phenomenon of swelling, and bring about the challenge of comparison with the frequently examined clay-organic compounds.

This report is concerned with the probable monolayer structure of tetracalcium aluminate hydrate which forms five hydration stages. A summary concerning configuration and properties of adsorption complexes with approximately 500 selected organic substances follows. As far as these substances are homologues of certain functional groups, the change of basal distances depends upon the number of C-atoms.

Aside from pure organic compounds, one can also form interlamellar complexes with a mixture of such compounds. Here again a rule of proportion between the number of C-atoms and the basal distance becomes evident. Another variant is the mixed interlamellar complexing of water with organic compounds and the re- and de-hydration reactions of these products.

The report discusses the bonding conditions of various functional organic groups to the inorganic lattice. Furthermore, a series of homopolar organic derivatives of the tetracalcium aluminate hydrates can be produced. As is known, the existence of such compounds of clay minerals is a subject of dispute.

## INTRODUCTION

CLAY mineralogy and the study of cement hydration have numerous points in common. In both fields, layer-structured crystals are the main object of investigation. Therefore it is of special interest that at least one product in hydrated cement, namely tetracalcium aluminate hydrate ( $C_4AH_x$ ),\* adsorbs organic compounds on the surfaces of its lamellae as certain minerals do. For cement scientists, these new reactions will be interesting because of the possible influence of the effects on known or prospective organic admixtures

\* As is usual in cement chemistry, the following symbolism is used; C = CaO; A =  $Al_2O_3$ ; H =  $H_2O$ ;  $C_4AH_x = 4CaO \cdot Al_2O_3 \cdot xH_2O$ .

to hydrating cement. Organic complexes of  $C_4AH_x$  as such can, in principle, be applied in a similar way to the known clay-organic complexes. Clay scientists have always looked upon the phenomenon of interlamellar adsorption under a more comprehensive aspect than that of clay mineralogy only: the first "hybrids between organic and inorganic chemistry" (Nahin, 1961, p. 259) were started from graphitic acid (Hofmann and Frenzel, 1930). Later on the pronounced difficulties in investigating clay-organic compounds encouraged the search for more simply constructed intercrystalline swellable model-compounds (MacEwan, 1960; see also Weiss, 1960). In this respect the tetracalcium aluminate hydrates are characterized by some outstanding qualities: (1) they are synthetic products of simple composition, which can be prepared easily in grain sizes suitable for X-ray powder diffraction; (2) they are the first known layer-structured crystals possessing neutral sheets that are capable of adsorbing water on the surfaces of their lamellae as well as neutral organic molecules; and (3)  $C_4AH_x$  structurally is closely related to a number of compounds incapable of interlamellar organic adsorption. There is a challenge to find out why one distinctive layer compound swells and related others do not. Work on this subject is underway. Here it must be emphasized that the study of a simply compounded neutral and yet swellable layer can elucidate considerably the process of intercrystalline swelling. It is known that counter-ions (cations and anions) between charged molecular sheets or molecular chains of swellable compounds may have more influence on the process of intercrystalline swelling than the chemical composition of the sheets or chains as such. The interlamellar adsorption of clay minerals and other known synthetic compounds is therefore a complicated process (Hofmann, 1960).

## EXPERIMENTAL PROCEDURES

### *Preparation of $C_4AH_x$*

The preparation of  $C_4AH_x$  can be done by different methods, as compiled by Turriziani (1964, pp. 234-5). In this paper, larger quantities of uniform consistency are prepared by solvation of Al in  $CO_2$ -free sodium hydroxide in a proportion corresponding to  $NaAlO_2$ . This solution is diluted to a concentration of about 0.4% NaOH and then treated with the stoichiometric quantity of CaO and shaken. Filtration is possible after 10 days of shaking. Adsorbed sodium hydroxide can be removed by washing with small quantities of cold water and finally three times with methanol. The product is dried in a vacuum desiccator over  $P_2O_5$ . After this treatment generally the hydrate  $C_4AH_{11}$  is obtained. In preparing  $C_4AH_x$ , extreme care is needed to exclude even traces of  $CO_2$ .

### *Preparation of Organic Complexes*

If the organic substances were liquid at room temperature, suspensions with  $C_4AH_x$  were prepared generally using the hydration stage  $C_4AH_{11}$ .

Solid organics were dissolved in ether, acetone, or acetonitrile. These solvents either do not react with  $C_4AH_x$  or need extremely long times of reaction. In individual cases (such as sugars, amino acids, etc.), water was used for this purpose.

*Preparation of Specimens for X-ray Diffraction*

The sodium alkali method of preparation provides a product of rather uniform grain size, hexagonal plates 10–20 microns in diameter, with oriented intergrowths of smaller crystals (Plate 1). The orientation parallel to (001) desired for X-ray analysis is obtained simply by spreading this material on the specimen holder.

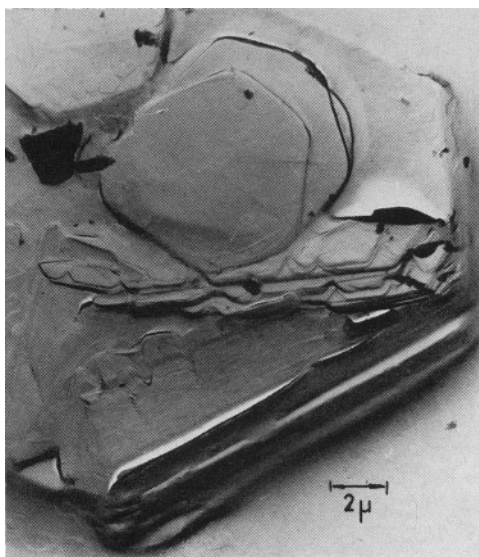


PLATE 1. Electron micrograph of tetracalcium aluminate hydrate; carbon replica.

Because of the extreme sensitivity of pure  $C_4AH_x$  to  $CO_2$ , a special procedure had to be developed. For this purpose a chamber connectible to a constant temperature control can be loaded in a glove box apart from the goniometer (Plate 2). On the bottom of the chamber there is a small bowl containing solutions to maintain defined water vapor atmospheres or organic vapor atmospheres. The lid of the chamber houses a ventilator and a measuring element for humidity and temperature (SINA Company, Zurich). The adsorption complexes of  $C_4AH_x$ , unlike the pure inorganic compound, predominantly are stable at the  $CO_2$  content of laboratory air. Thus the preparation in the glove box frequently is not necessary. The experimental temperatures were  $25^\circ C$ , unless otherwise indicated.

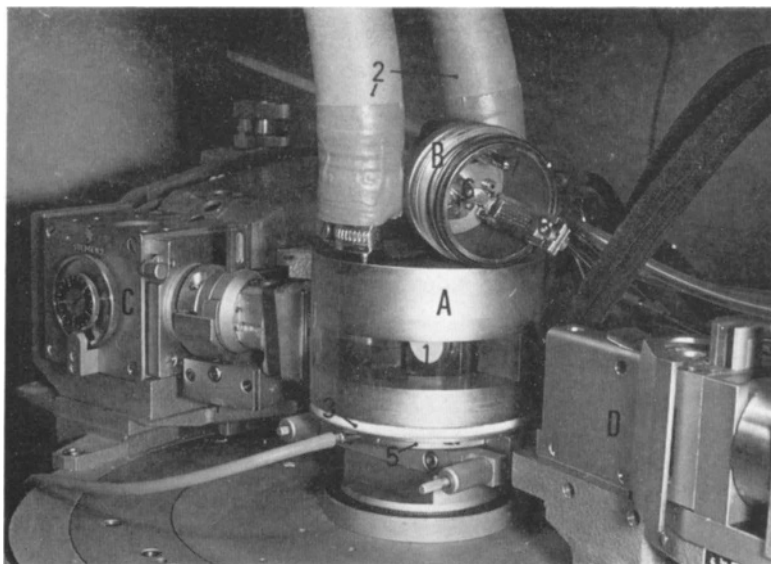


PLATE 2. (A) Removable X-ray climate chamber with: 1, specimen; 2, connection to constant heat control; 3, teflon-disc as gasket; 4, semi-cylindrical foil; 5, water-cooled base. (B) Lid with: 6, ventilator; 7, Hg-thermometer; 8, measuring element for temperature and humidity control. (C) X-ray tube. (D) Counter tube.

## TETRACALCIUM ALUMINATE HYDRATES AND RELATED COMPOUNDS

### *Tetracalcium Aluminate Hydrates*

*Hydration stages.*—Figure 1 shows that there are five exactly defined hydrates of  $C_4AH_x$  with  $x=7, 11, 12, 13$  and  $19$ , corresponding with basal reflections of  $7.2, 7.4, 7.9, 8.2$  and  $10.6 \text{ \AA}$  (zur Strassen and Dosch, 1965).

*Structure.*—The structure of  $C_4AH_x$  is not definitely known. Different proposals for the structure have been made (Turriziani, 1964, pp. 246–7), but only the proposal by Buttler, Dent Glasser, and Taylor (1959) sufficiently explains the experimentally measured lattice constants. In this concept the pseudo-cell is only one octahedral layer thick, and similar in its construction to portlandite,  $Ca(OH)_2$ . Figure 2 shows a portlandite layer in which one-third of the Ca-positions are replaced by Al. The small circles stand for Al, the medium-sized ones for Ca, and the large circles for OH-ions which surround the cations octahedrally. The Al-ions maintain a complete residual affinity in this arrangement symbolized by “+”. For that reason the Al-ions need an additional seventh OH for neutralization, which is situated in the gaps on the OH-layer, directly above the Al-positions. There is a strong probability that the seventh OH is ordered, or statistically distributed, on both

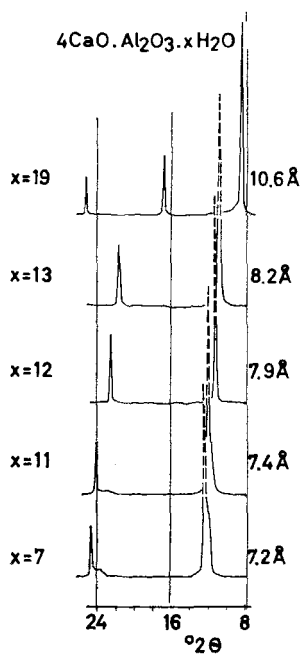


FIG. 1. Hydration stages of  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

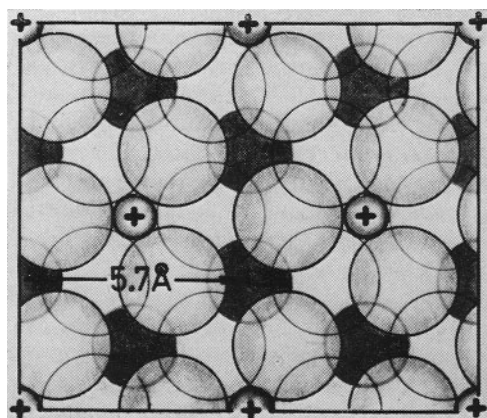


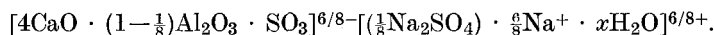
FIG. 2. Section of a  $\text{C}_4\text{AH}_x$ -layer  $1c$ ; "outside"-OH not shown.

sides of the layer. Therefore, the whole layer is symmetrically structured and fully neutralized.

### *Related Compounds*

*Compounds also possessing neutral sheets.*—The special placement of the seventh OH in the structural element  $[\text{Ca}_2\text{Al}(\text{OH})_6][(\text{OH}) \cdot x\text{H}_2\text{O}]$  of  $\text{C}_4\text{AH}_x$  leads to the possibility of its replacement by other anions like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and so on. However, these reactions are not reversible. In this way, one can find new compounds like  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot x\text{H}_2\text{O}$ , the so-called “monosulfate”, all of which are of importance in cement hydration. None of these substitution products show the phenomenon of interlamellar adsorption of organic compounds, but they possess different hydration stages.

*Compounds with negatively charged sheets (“alkali-monosulfate”).*—It should be of special interest to clay scientists that one can transform monosulfate—and only monosulfate—to a substance with negatively charged sheets. This decomposable substance is only stable in the presence of high concentrations of sodium sulfate and aluminate and can only be isolated jointly with its mother-liquor. By means of Schreinemaker’s analysis of residues (Dosch and zur Strassen, 1966) and later by means of ion-exchange experiments in which alkali could be replaced from  $\text{Li}^+$  to  $\text{Cs}^+$  and also by quaternary alkyl-ammonium bases (Dosch, 1966), the following formula was established:



The formula shows that this substance is composed of negatively charged layers. However, it is still uncertain whether or not alkali sulfate is actually situated in the interlayer.

On the occasion of my visit to the laboratories of the Portland Cement Association, Skokie, Illinois, in October 1966, Nathan R. Greening informed me that he had discovered the new compound too. He also considered it a calcium aluminate sulfate hydrate containing sodium.

A comparison of the qualities of the structurally closely related compounds mentioned above reveals the following situation:

1.  $\text{C}_4\text{AH}_x$  consists of neutral sheets and shows an extreme capability for the interlamellar adsorption of neutral organic compounds.
2. Simple substitution products such as monosulfate also consist of neutral sheets, but do not show any interlamellar organic sorption.
3. The newly discovered substance (alkali-monosulfate) consists of negatively charged layers and shows ion-exchange for alkali and organic cations. Neutral organic molecules are not adsorbed.

Subparagraph 3, above, is related to the reactions of clay minerals with onium-complexes. As indicated before, the reasons for the absence of interlamellar organic adsorption of substances listed in subparagraph 2 will be the subject of future work. The following paragraph explains subparagraph 1 above, the interlamellar adsorption of neutral organic molecules on tetra-calcium aluminate hydrate.

ORGANIC ADSORPTION COMPLEXES OF  
TETRACALCIUM ALUMINATE HYDRATE*Homologous Series*

To obtain a general view of the extent of intercrystalline reaction of  $C_4AH_x$ , the adsorption complexes of numerous selected organic compounds were prepared and the one-dimensional swelling in the direction of the *c*-axis measured by X-rays. In this connection, those classes of organic compounds that form homologous series, like alcohols, fatty acids, etc., are particularly instructive. Figure 3 shows the basal distances of the complexes of  $C_4AH_x$ ,

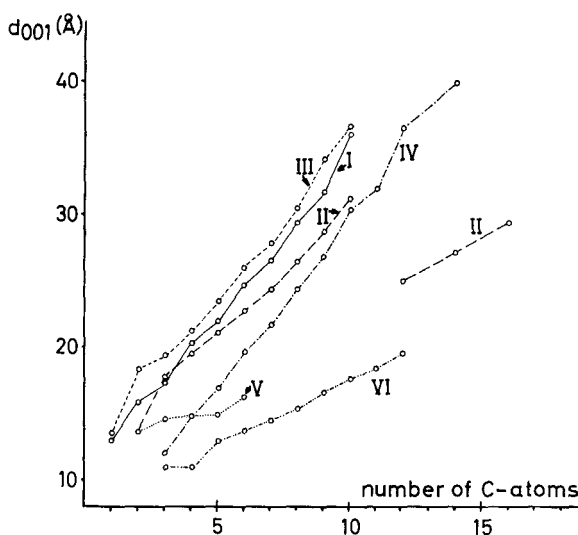





FIG. 3.  $C_4AH_x$ -complexes with several homologous organic classes: I, alcohols; II, mercaptans; III, amines; IV, fatty acids; V, difunctional alcohols (glycols); VI, dicarboxylic acids.

dependent upon the number of C-atoms, for some different homologous organic classes. Generally, the basal distances increase in roughly linear relation with the number of C-atoms within one homologous class. At the same time there are exceptions, for instance with the mercaptans, where the basal distance increases from  $C_{12}$  to  $C_{16}$  are markedly lower than those for the series with  $C_2$  to  $C_{10}$ . Besides steep curves, there are other curves rising at lower rates (V and VI), finally (not shown in Fig. 3) constant basal distances at 10.5 to 11.5 Å and also at 13.5 to 15.0 Å. These constant basal distances can occur during the adsorption of numerous and also dissimilar compounds.

TABLE 1.—BASAL DISTANCES OF ALCOHOL-C<sub>4</sub>AH<sub>x</sub>-COMPLEXES

Alcohol	Basal distance (Å)	Difference (Å)
CH <sub>3</sub> · OH	12.90	_____ 2.8
CH <sub>3</sub> · CH <sub>2</sub> · OH	15.72	_____ 1.7
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>2</sub> · OH	17.40	_____ 2.8
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>3</sub> · OH	20.20	_____ 1.8
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>4</sub> · OH	22.00	_____ 2.7
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>5</sub> · OH	24.66	_____ 1.8
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>6</sub> · OH	26.56	_____ 2.7
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>7</sub> · OH	29.28	_____ 2.5
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>8</sub> · OH	31.77	_____ 4.4
CH <sub>3</sub> · (CH <sub>2</sub> ) <sub>9</sub> · OH	36.19	
 · CH <sub>2</sub> · OH	20.60	
 · CH · OH	10.68	
 · CH · (CH <sub>2</sub> ) <sub>2</sub> · OH	10.6 > 20.8	

The curves in Fig. 3 present a number of data from which a more detailed arrangement of the organic molecules can be derived. The following is to explain this for the example of alcohol complexes. The curve (I of Fig. 3) is a zigzag line. Table 1 indicates that the increases of the basal distances from C<sub>even</sub> to C<sub>odd</sub> amount to 1.8 Å, from C<sub>odd</sub> to C<sub>even</sub> to 2.8 Å. The corresponding points for C<sub>even</sub> and C<sub>odd</sub> can be connected by two parallel straight lines. The alcohols, C<sub>9</sub> and C<sub>10</sub>, deviate to higher basal distances.

The average increase of basal distances for the complexes with the alcohols C<sub>1</sub> to C<sub>8</sub> (linear range) is  $\Delta d_{001}/\Delta n = 16.38/7 = 2.34 \text{ Å/C-atom}$  for two subsequent alcohols. In the longitudinal axis of zigzagged carbon chains, however, the C—C distance is only 1.27 Å. This distance being smaller than the experimentally obtained value of 2.34 Å suggests that each two alcohol molecules are arranged one behind the other in their longitudinal axis, and form a specific angle with the inorganic surface. The sine of the angle is  $\sin \zeta = 2.34/2 \times 1.27$ ;  $\zeta = 67^\circ$ . The inclination of this angle can not be accurately quoted.



Further information is provided by the profiles of X-ray diagrams. The odd-order intensities of  $00l$ -reflections are enhanced, those of even orders weakened. This intensity relation has a known cause and can also be observed on pure crystallized alcohols, fatty acids, etc. The terminal  $\text{CH}_3$ -groups of successively arranged carbon chains cannot come closer to each other than approximately  $3.5 \text{ \AA}$ . This way a minimum of density is reached  $\perp c$  shown in the intensities of  $00l$ -reflections.

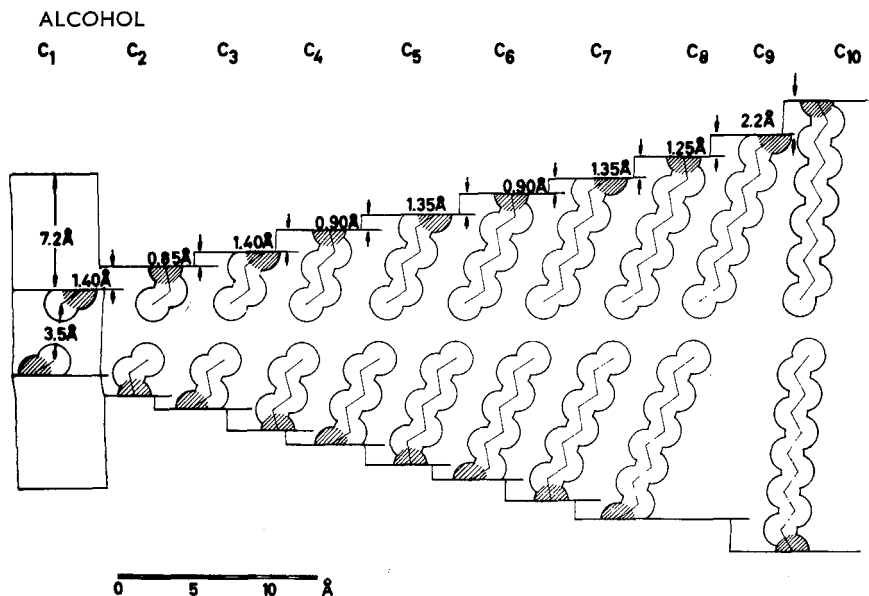


FIG. 4. Explanation of the alternating basal increases for the alcohol complexes  $C_1$  through  $C_{10}$ ; H-bonding not considered.

In addition, the amount of adsorbed molecules can be determined, for instance by determining the smallest quantity of organic material needed to make the lines of non-converted  $C_4\text{AH}_x$  disappear. Because of the low stability of alcohol complexes, these measurements of course are not precise. Values of 4 to 5 moles alcohol/mol  $C_4\text{AH}_x$  are obtained. In the  $C_4\text{AH}_x$ -layer the area of one "molecule"  $C_4\text{AH}_x$  is about  $56 \text{ \AA}^2$ . According to Weiss (1961) the area of a straight alkylchain is approximately  $21 \text{ \AA}^2$ . Therefore, 4 molecules of alcohol per  $C_4\text{AH}_x$  already form a densely packed arrangement, wherein the alcohol molecules are arranged with their longitudinal axis in the inclination angle, two of them sitting above and two below the inorganic layer.

Figure 4 shows the arrangement of the ten different alcohols in the  $C_4\text{AH}_x$ -complexes resulting from the preceding explanations. The sequence

$$2 \times (\dots 1.4 \dots 0.9 \dots 1.4 \dots) \text{ \AA}$$

from one alcohol to the next homologue coincides exactly with the experimentally obtained data (Table 1), and results from the zigzag shape of the chains and the inclination angle.

However, this model must be improved if we assume H-bonding between alcoholic and inorganic OH-groups. In fact it is not understood why the H-bonding should be directed against the inorganic layer alternating between high and low angles depending on the C-number. The necessary refinement will not be discussed here in detail. However, a satisfactory model for adsorption complexes is acquired if we consider that the inorganic layer is of uneven thickness because of the "seventh" OH-ions protruding to the outside. Obviously alcohol molecules can bond both octahedral and "outside" or "seventh" OH-ions. For further information see Dosch (1967).

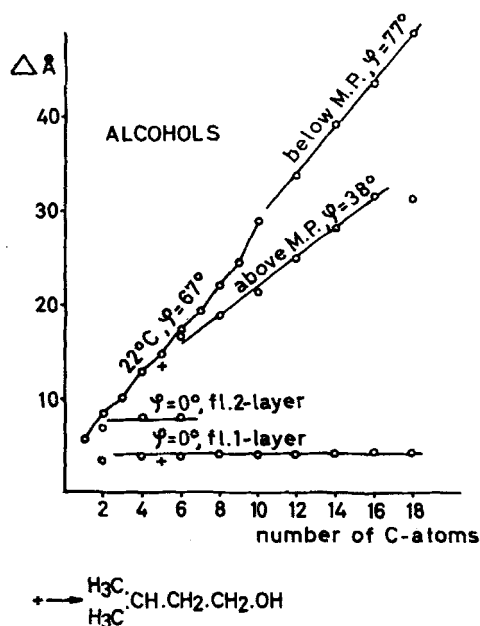


FIG. 5. Comparison of alcohol-complexes of  $C_4AH_x$  and of montmorillonite (according to Brindley and Ray, 1964).  $\Delta \text{Å}$  = measured basal distances minus thickness of the inorganic layers (7.2 Å for  $C_4AH_7$ , 9.7 Å for Ca-montmorillonite).

The elongation of the curve of the alcohol complexes toward C=zero (that is,  $H_2O$ !) indicates a basal distance of approximately 11 Å, concurring closely with the value 10.6 Å of  $C_4AH_{19}$  (Fig. 1) ( $H_2O$ -double layer).

Figure 5 compares the alcohol complexes of  $C_4AH_x$  with the corresponding montmorillonite complexes according to Brindley and Ray (1964). Attention is invited to the altered scale of the ordinate. With montmorillonite one can

find four different kinds of interlayering: one-layer complexes and two-layer complexes with the chain molecules parallel to the silicate surface, and two series of long-spacing complexes forming different inclination angles above and below the melting point (M.P.) of the alcohols. The montmorillonite curve below the melting point continues reasonably the curve referring to tetracalcium aluminate hydrate.

Isomeric alcohols are adsorbed much more hesitantly than the straight-chained ones, and in general only as a flat single layer (basal distances 10.6 to 10.7 Å, Table I and Fig. 5). Steric hindrance is certainly the main cause of this. I-amylalcohol (C<sub>5</sub>) forms both a flat layer arrangement, and to a lesser extent, steep double chains. The corresponding basal distance of 20.8 Å is the mean value between those of the neighbouring straight-chained homologues.

#### *The Main Forms of Interlayering*

In the preceding example of alcohols a molecular arrangement, the steeply inclined double-chain, was derived from X-ray data. The following presents briefly, the other identified forms of interlayering. Figures 6 through 11 each show one X-ray diagram of a typical complex with the formula of the corresponding adsorbed molecule and the resultant basal expansion. The left-hand part of each figure shows a diagram of the organic molecules (thick lines) between the inorganic layers (shaded). Under the heading, "moreover", the most important classes of organic compounds which are adsorbed with the same arrangement are listed. Please note the sharp peaks.

*Figure 6.*—Special example: D-malic acid ( $d_{001} = 11.22 \text{ \AA}$ ). The organic molecules form a one-layer complex with the longitudinal axis of the molecules parallel to the inorganic surface. Under "moreover", the other hydroxy acids, polyvalent alcohols (mannitol, etc.), various sugars (monoses, disaccharides), and acid amides are listed. As to their bonding strength to the inorganic layer these substances are extremely differentiated: the acid amides are only loosely bonded, whereas the others, because of their numerous hydroxyl- and/or carboxyl-groups, are strongly bonded to the inorganic OH-groups.

*Figure 7.*—X-ray diagram: complex with ethylene glycol. Configuration: Flat two-layer complex. As a result of the repulsion between organic molecules, a minimum of density is reached perpendicular to *c*; this is verified by the X-ray diagram where the odd-order basal reflections are intensified and the even-order ones are weakened. Moreover: the homologous glycols ( $\alpha$ ,  $\omega$ -dialcohols), glycerine, some amino acids, and the like.

*Figure 8.*—Certainly this minimum of density shown in Fig. 7 is not mandatory. For hemimellitic acid ( $d_{001} = 14.57 \text{ \AA}$ ) the intensities of basal reflections decrease regularly, according to the polarization factor. In this case probably all three carboxyls are bonded, and the chair-shaped benzene nuclei form an overlapping arrangement.

*Figure 9.*—X-ray diagram: complex with 1,10-decanedithiol. Each of the terminal groups of this straight molecule is bonded to one of the opposing

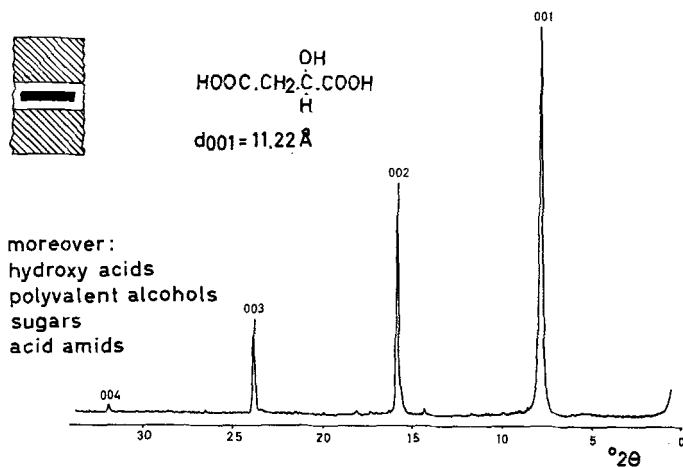


FIG. 6. Flat single-layer complexes.

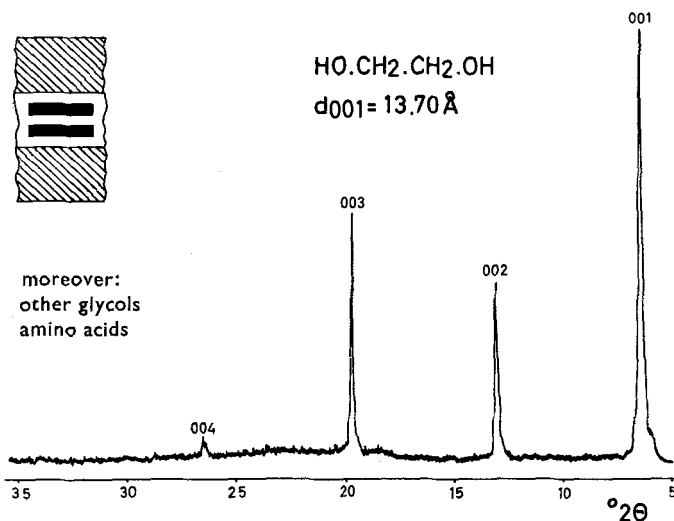


FIG. 7. Flat two-layer complexes (with density minimum).

inorganic layers, forming a high angle of intersection. The splitting of basal reflections indicates two competing arrangements with small differences in their inclination angles. Moreover: the homologous dithiols, dicarboxylic acids and diamines.

*Figure 10.*—X-ray diagram: complex with  $\alpha$ -naphthoic acid. Configuration: steeply inclined double molecules. Density minimum  $\perp c$ . This type has been

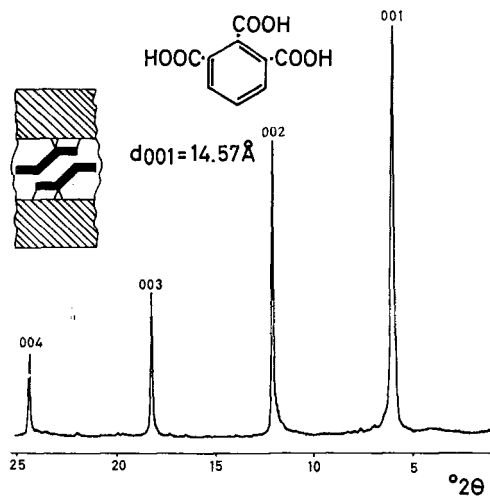


FIG. 8. Two-layer complex without density minimum.

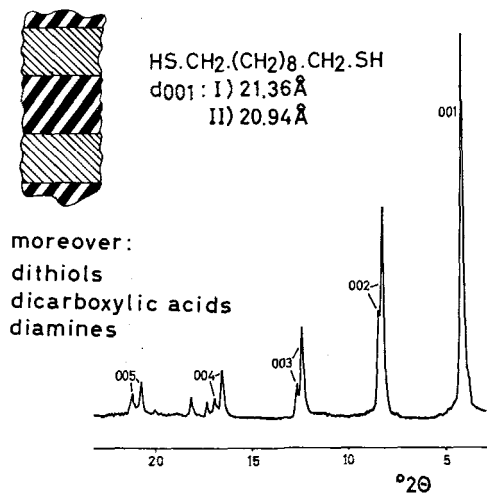


FIG. 9. Complexes with chain molecules bonded to the inorganic surface with two terminal functional groups.

previously dealt with in detail, within the discussion of the alcohol complexes.

Figure 11.—X-ray diagram: complex with 1-decanethiol. Configuration: like Fig. 10, minimum of density, however, not pronounced. To understand the difference between Figs. 10 and 11, one must realize that the inorganic

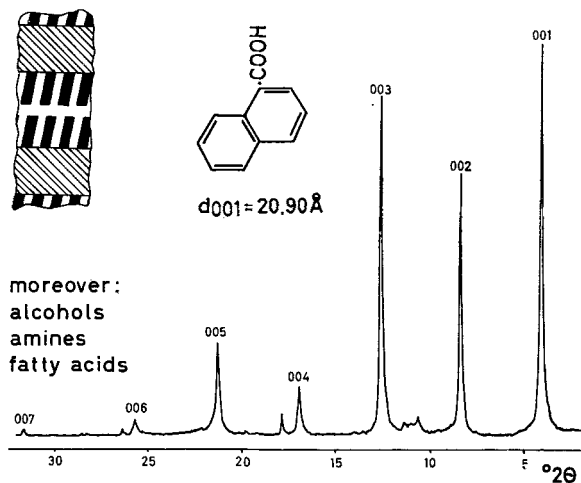


FIG. 10. Complexes with steeply arranged double molecules (with density minimum).

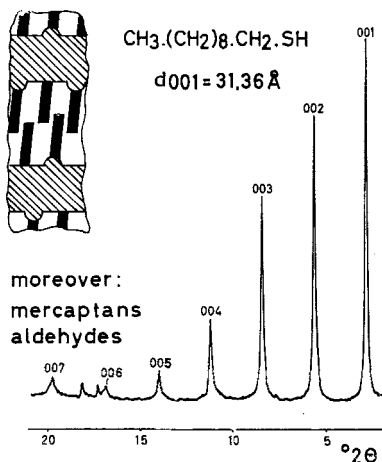


FIG. 11. Complexes with steeply arranged double molecules (without density minimum).

layers are not entirely plane but partially uneven because of the protruding OH-ions. Likewise there are probably types of adsorption that can take place either on the octahedral or the "outside" OH, also types where the molecules do not discriminate between the two sorts of OH-ions. In the latter case one can imagine a form of interlayering as shown here schematically, in a way that the organic molecules overlap each other.

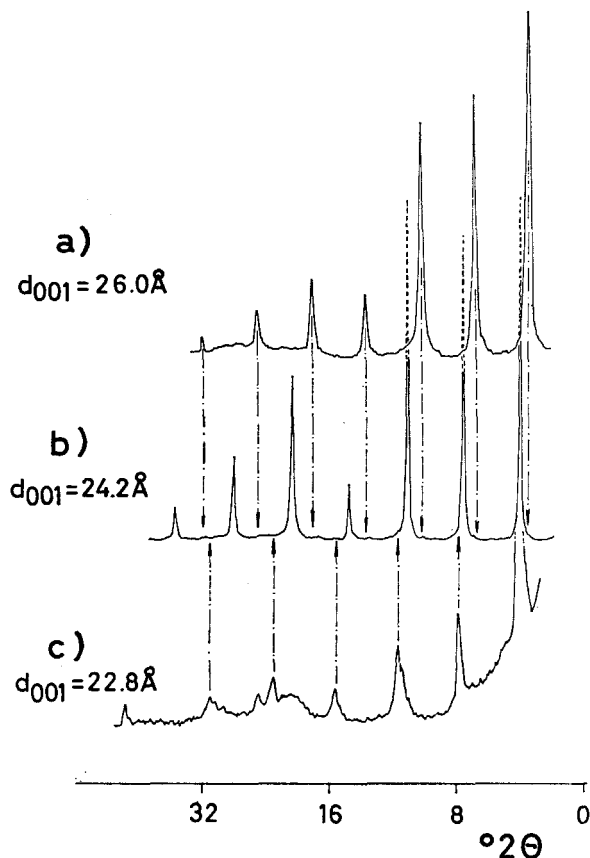


FIG. 12. Sorption complexes with one and with two organic compounds: (a) with *n*-hexylamine; (c) with phenylacetic acid; (b) with a 1:1 mixture of both organics.

These examples show a restriction of the intercrystalline adsorption of  $C_4AH_x$  to neutral polar molecules. It is striking that organic substances with extremely high dielectric constants, such as nitromethane or acetonitrile, are not adsorbed by  $C_4AH_x$ . Instead, they are adsorbed by montmorillonite in the form of flat three-layer complexes (MacEwan, 1948). This differing behavior is based on the differences of the electric field in layer structures with a net charge (montmorillonite) and neutral layer structures ( $C_4AH_x$ ).

#### *Binary and Ternary Adsorption*

Besides homogeneous adsorption,  $C_4AH_x$  also can interlayer in ordered arrays two or more types of organic molecules at the same time. Figure 12

shows the mixed complex with a 1:1 mixture of hexylamine + phenylacetic acid (center) between the complexes of the two pure organic components.

Figure 3 indicates that with  $C_4AH_x$ , the adsorption of homologous straight-chained molecules in general does not exceed a chain length of approximately ten C-atoms. With montmorillonite, on the other hand, it is mostly the long molecules that have preference over the shorter chains. In Fig 5. the curve of alcohol-complexes below M.P. does not start before alcohol- $C_{10}$

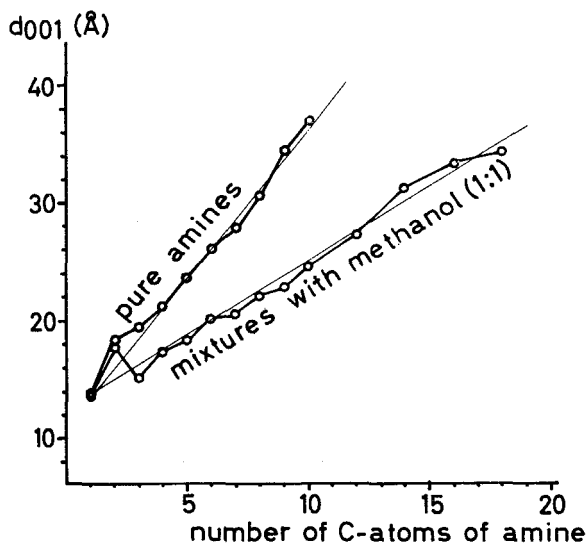


FIG. 13. Adsorption of amines and mixtures of amines with methanol.

$C_4AH_x$ , which is already carrying short-chained molecules, can also adsorb—in a second step of adsorption—molecules with C-numbers exceeding 10. As an example for the binary mixed adsorption of a homologous series, Fig. 13 demonstrates the adsorption of amines in the presence of methanol. Pure amines are only adsorbed up to and including  $C_{10}$ . Compared to this in mixture with methanol, the adsorption continues up to amine- $C_{18}$ . In both cases the molecules are steeply inclined, forming double chains. The faint lines indicate the theoretical basal distance both for the case of mixed adsorption with the assumption that amine and methanol molecules are superposed, and for the case of homogeneous adsorption, presuming two identical superposed amine molecules.

Figure 14 illustrates the more complicated processes in the ternary adsorption of mixtures of benzene, benzoic acid and fatty acids  $C_nH_{2n+1}COOH$  with  $n=8$  through 20 as a variable component. The arrows indicate the



direction of changes of basal reflections for repeated X-ray diagrams at different times. During the X-ray examination, the liquid benzene initially present in excess evaporates, and the basal distances of ternary complexes—the upper dashed line—drop to the level of the medial dashed line. The basal distances again reach the initial higher values when the substances are

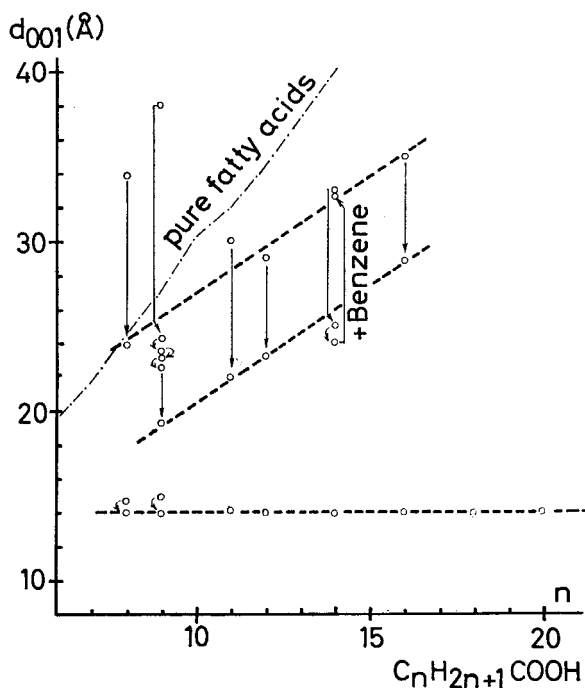


FIG. 14. Ternary adsorption complexes.

rewetted with benzene; this proves that the shrinkage of the lattice is in fact caused by the loss of benzene. The other evidence, that each two different acids are taking part in the complexes, follows from comparison with the complexes of pure fatty acids (faintly dashed line). In addition, all diagrams reveal a constant  $00l$ -sequence with  $d_{001} \sim 14 \text{ \AA}$ .

#### INFLUENCE OF WATER VAPOR PARTIAL PRESSURE AND TEMPERATURE

Most adsorption complexes, both with pure and with mixed organic adsorbents, moreover can adsorb different quantities of water, dependent upon the outer  $p_{H_2O}$ . In the same way nonpolar organic compounds, like hydrocarbons, can be adsorbed in the presence of polar organic molecules.

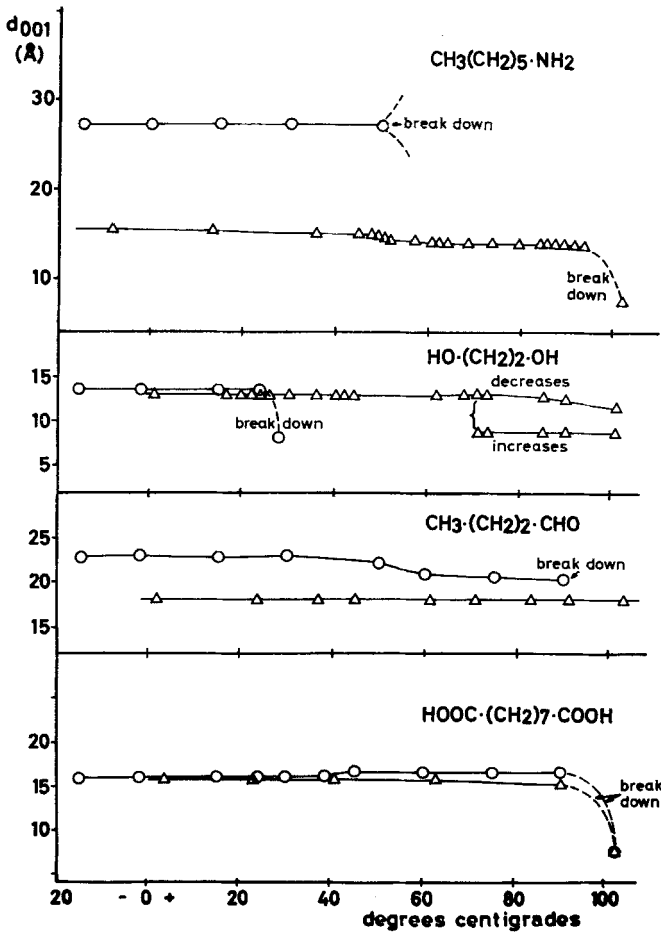


FIG. 15. Influence of temperature and  $p_{H_2O}$  on some different adsorption complexes; circles: over 100% R.H.; triangles: over  $P_2O_5$ .

The influence of the outer water vapor atmosphere, and of the temperature on different adsorption complexes, is illustrated by Fig. 15. Within the temperature range  $-20$  to  $+100^\circ C$  the following  $C_4AH_x$ -complexes were X-rayed each after drying over  $P_2O_5$  (triangles) and at 100% relative humidity (circles): (a) hexylamine (configuration as in Fig. 10), (b) ethylene glycol (as in Fig. 7), (c) butyric aldehyde (as in Fig. 11), and (d) azelaic acid (as in Fig. 9).

At 100% R.H. the basal distance of hexylamine- $C_4AH_x$  is larger than when dry. The same applies for butyric aldehyde, although less pronounced. With

increasing temperature at 100% R.H., the complexes of amine and of glycol break down sooner than the complexes of the acid and the aldehyde. Over  $P_2O_5$  also the complexes with hexylamine and glycol remain stable up to higher temperatures. For the amine, the aldehyde, and the acid, each one of the curves shows a slight break that indicates reorientation of the organic molecules. For the glycol dried over  $P_2O_5$ , beginning with  $70^\circ C$ , a complex with the extremely low basal distance of  $8.8 \text{ \AA}$  is formed. The amount of this complex increases with rising temperature.

### BONDING CONDITIONS; ALKYLATION OF TETRACALCIUM ALUMINATE HYDRATE

The adsorption processes take place on a coherent surface of inorganic OH-ions. In the case of alcohols, amines, and so on, H-bonding must be presumed. The reactions of  $C_4AH_x$  with aldehydes, organic acids, and mercaptans are strongly exothermic. Here it is probably rather stable homopolar bondings that occur between inorganic and organic partners, esterifications and the like.

The most interesting example of a true homopolar bonding is the methylation or ethylation of  $C_4AH_x$  with dialkylsulfates in an alkaline medium. In alkylated  $C_4AH_x$  one can again adsorb on the surfaces of its lamellae a large number of organic compounds.

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