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ADSORPTION AND RETENTION OF AN ORGANIC MATERIAL BY MONTMORILLONITE IN THE PRESENCE OF WATER*

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Abstract

The adsorption of a polyethylene glycol ester of oleic acid on montmorillonite is studied in relation to the water content of the system. At low concentrations of organic material to clay mineral, 70% of the organic material is adsorbed on the clay and 30% remains in solution. The lattice spacings of the clay-organic complexes, when dried at 110° C., are studied for clays saturated with Na, Ca and Mg ions. Ordered complexes are found containing one layer or two layers of organic material between silicate layers, and in the appropriate composition ranges mixtures of 1-layer and 2-layer types are observed rather than mixed sequences. Repeated washings reduce 2-layer to 1-layer type sequences, but a single organic layer between silicate sheets is firmly held.

Introduction

The adsorption of organic molecules by montmorillonite and the resultant expansion of the crystalline lattice have been intensively studied and general surveys have been given by MacEwan (1951) and by Grim (1953). These studies have been made mainly with liquids, either organic liquids or solutions in water, but in a few instances with organic vapors. Glaeser and Mering (1952, 1954), and Barrer and MacLeod (1955) have studied the adsorption and desorption isotherms of montmorillonite for a number of gases and vapors in relation to the relative vapor pressure; comparable studies for organic materials dissolved in water appear not to have been made.

In the present investigation an attempt has been made to study equilibrium in a system comprising montmorillonite, an organic material, and water. In particular, attention has been given to (i) the partition of the organic material between the clay and the liquid phase, (ii) the change in character of the clay-organic complex as the organic com-

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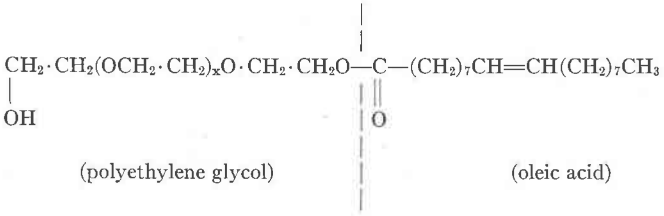
ponent is increased from small amounts up to saturation, and (iii) the retention or fixation of the organic material by the clay.

In recent years much attention has been given to the adsorption of cationic organic complexes on clays (see Gieseking (1939), Hendricks (1941), Jordan (1949, 1954), Franzen (1955), Talib-Udeen (1955), Barrer and MacLeod (1955), Haxaire and Bloch (1956)). The results indicate that in addition to a cation exchange reaction, physical adsorption processes also occur. It seemed desirable, therefore, to study the adsorption of a non-ionic complex before considering situations in which exchange reaction take place.

MATERIALS

Organic material

The experiments have been carried out with a commercial wetting agent, "Nonisol 250", supplied by the Geigy Chemical Corporation, the choice of which was partly fortuitous. This is an ester of polyethylene glycol and oleic acid, with the following chemical formula:



$$\underset{\displaystyle OH}{\underset{|}{CH_2}}\cdot CH_2(OCH_2\cdot CH_2)_xO\cdot CH_2\cdot CH_2O-\underset{\displaystyle O}{\underset{\|}{C}}-(CH_2)_7CH=CH(CH_2)_7CH_3$$

The material is normally a paste, readily soluble in water and in most organic solvents. It is recoverable from solution in water by drying at 105° C. with less than a 1% weight loss, and with no significant change in the *x*-ray powder diagram. The material is therefore chemically stable to solution in water and re-drying.

Clay material

Montmorillonite has advantages over non-swelling clays since the expansion of the crystal lattice can be measured by *x*-rays and this provides an accurate method of studying adsorbed surface layers which is not applicable to the non-swelling clays.

A purified Wyoming bentonite was supplied by Dr. J. L. McAtee, of the Baroid Sales Division, National Lead Company, Houston, Texas. This is a relatively well-crystallized form of montmorillonite. The precise purification process is not known but is believed to be one of sedimentation and/or centrifugation. The sample supplied had Na and Ca ions as exchangeable cations and contained a trace of cristobalite impurity.

EXPERIMENTAL PROCEDURES

Clay mineral preparation

By repeated treatment with 1-N solutions of the respective chlorides, clay samples were prepared saturated with Ca, Na and Mg ions. Following sedimentation and repeated washings of the clays with distilled water, the remaining traces of excess chloride were removed by dialysis through cellophane tubing, using the silver nitrate test. The clay samples were then dried in air at 110° C. and stored in a dessicator over activated alumina.

Clay-organic adsorption procedure

The experiments were designed mainly on a volumetric basis. A suspension of montmorillonite containing 1 gm. clay/liter water, and an organic solution containing 1 gm./liter water were prepared. Requisite volumes of clay suspension, organic solution, and water were mixed and agitated intermittently for 4 hours. After centrifugation, an aliquot of the clear solution was analysed for organic material, and the clay was removed for *x*-ray examination.

Organic analysis

To determine the organic matter left in solution, a direct weighing method was tried using very thin Pyrex bulbs as evaporating dishes. The method was found to be capable of giving reasonable accuracy but was very inconvenient.

A titration method was developed making use of the C=C bond in the oleic acid part of the molecule. Adsorption of bromine by the double bond was determined by measuring excess bromine with a thiosulphate titration. A calibration curve was obtained using organic solutions of known concentration. The conditions for the bromine absorption and the subsequent titration were standardized precisely. The method was found to be accurate and measurements could be repeated.

X-ray analysis

The clay samples were prepared as thin, oriented layers on glass slides and were examined with a Philips Norelco diffractometer with CuKα radiation. The atmosphere surrounding the specimen was controlled by air circulation, either dry air or air of humidity approaching 100%. The latter was used with wet clay films prior to any drying treatment and ensured that the clay film remained wet during the *x*-ray examination, usually about 30 min.-1 hr.

RESULTS

(a) *Partition of organic material between clay and water for constant initial concentration of organic material*

The three components, clay, organic material and water, were mixed to provide an initial concentration of 300 mg. organic material/liter water, and to cover a range of values for the ratio of organic material to clay.

In Fig. 1, the organic material adsorbed per gm. clay is plotted against total organic material in the system per gm. clay. The adsorption curve tends smoothly to an asymptotic limit of about 0.6 gm. adsorbed organic material per gm. clay. In the region of about half maximum adsorption a large number of observations were made to check for a possible departure from the smooth curve, but within the accuracy of the determinations, no deviations were found.

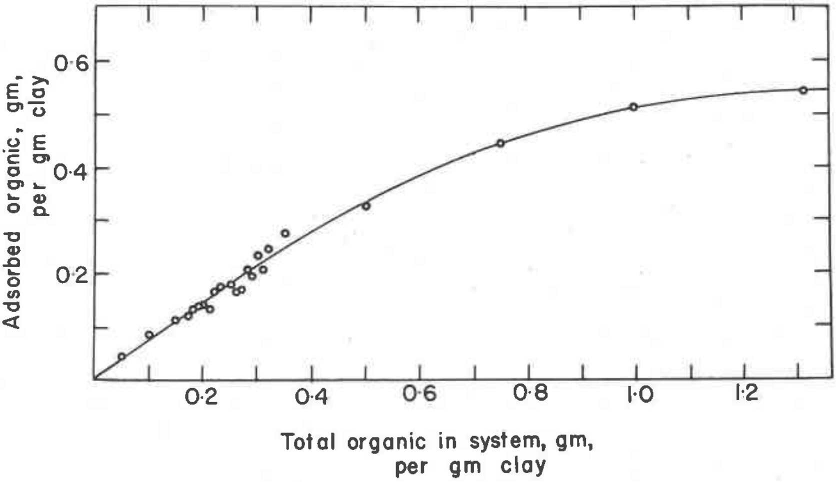


FIG. 1. Adsorption of polyethylene glycol ester of oleic acid on montmorillonite in an aqueous system.

Up to about 50% of maximum adsorption, the curve is linear with a gradient corresponding to about 70% of the total organic material being adsorbed on the clay. At about 90% of maximum adsorption, the clay adsorbs about 50% of the total organic material.

(b) *X-ray examination of the wet clay-organic films prior to drying*

After centrifugation, the clear liquid was drained from the clay, a few ml. of water were added, and several drops of the clay suspension placed on a glass slide. Evaporation in air was allowed to proceed until a coherent but still moist clay film was obtained. This was placed in the diffractometer enclosure and kept moist by passing air of almost 100% R.H.

The lattice spacing $d(001)$ was 18.5–19 Å largely irrespective of the exchangeable cations and the amount of adsorbed organic material. The results are set out in Table 1. For Na-montmorillonite, the spacing ranged up to 22 Å for small quantities of adsorbed organic material, but otherwise conformed to the values found for Ca- and Mg-montmorillonites. These results suggest that prior to drying the lattice spacing is determined principally by water remaining between the silicate sheets.

TABLE 1. LATTICE SPACINGS OF WET MONTMORILLONITE FILMS CONTAINING ADSORBED POLYETHYLENE GLYCOL ESTER OF OLEIC ACID (NONISOL 250); VALUES OF $d(001)$ IN Å

Exchangeable cations	Na	Ca	Mg
Clay films prior to any drying treatment	18.0–22.0	18.6	18.8–19.2
Clay films re-wetted after drying at 110° C.	18.4–19.6	18.4–18.8	18.4–19.0

(*c*) *X-ray examination of the dried clay-organic films*

The clay-organic films were now dried at 110° C. and maintained in a dry atmosphere during storage and during *x*-ray examination with the diffractometer.

The results vary according to the exchangeable cation and the total organic/clay ratio. Typical diffractometer recordings for selected organic/clay ratios are shown in Figs. 2, 3, and 4, and the lattice spacings, $d(001)$, are shown in Figs. 5, 6, and 7.

Figs. 5, 6, and 7 show that the lattice spacing expands to nearly stationary values of about 14 Å and 17.5 Å as the total organic content is increased. The detailed results, see Table 2, show that the mean lattice expansions with respect to clays dried at 250° C. and without organic material are 4.20 Å and 7.70 Å. These expansions are regarded as corresponding to one and two layers of organic material respectively between the montmorillonite sheets.

It is of particular interest to consider whether, with increasing organic content, the clay-organic complexes form regular structures at certain compositions, and irregular or interstratified structures at intermediate compositions. The evidence in Figs. 2–7 points to the formation of regular structures as the main feature of these organic complexes. Although there is some evidence for irregular stratifications of the clay-organic layers, this does not appear to be a major characteristic of the present system.

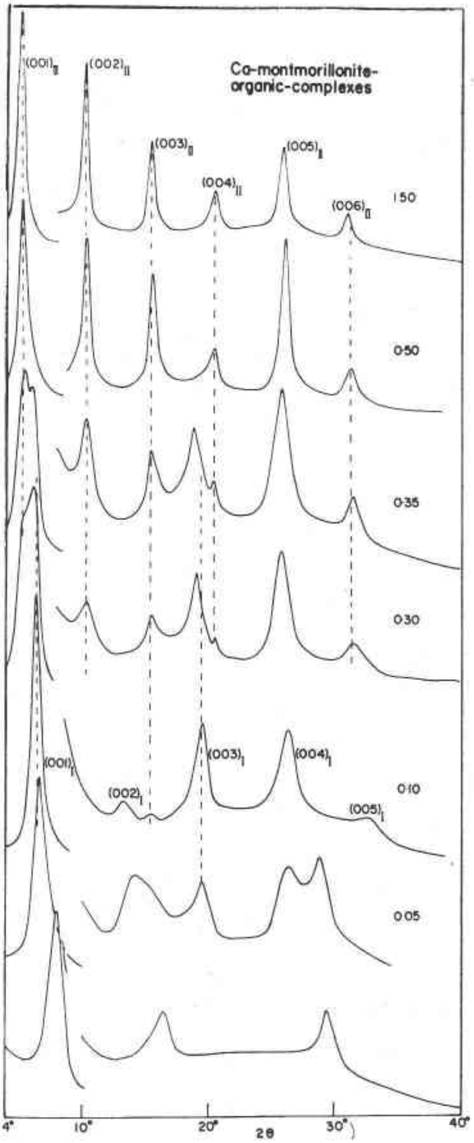


FIG. 2. Diffractometer recordings of Ca-montmorillonite-organic complexes. The ratio of total organic material in the system to the amount of clay is shown by the value at the right hand side of each diagram.

The breaks in the curves at about $2\theta = 10°$ arise from a change of the intensity scale for the higher order reflections.

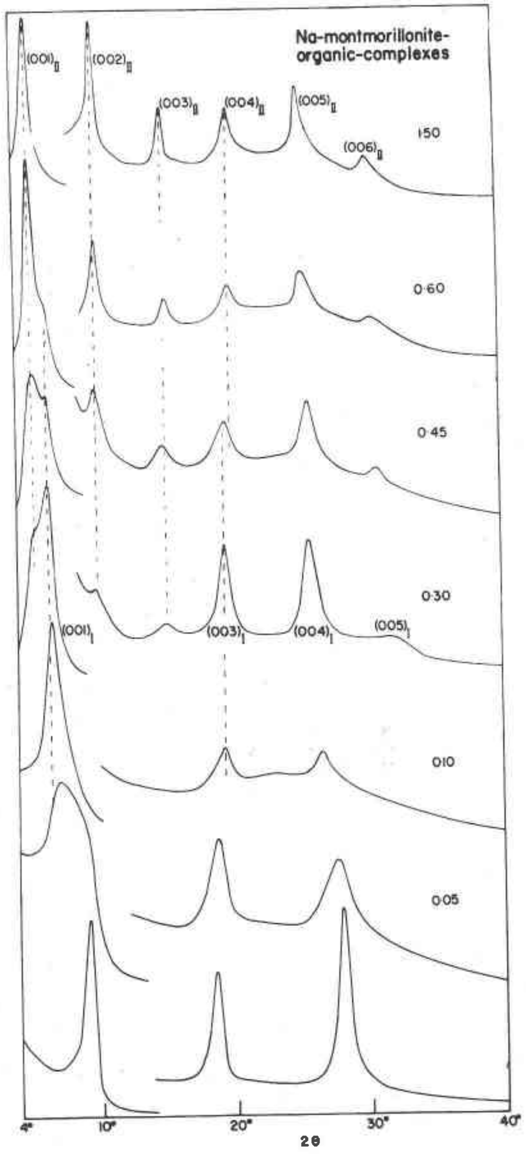


FIG. 3. Diffractometer recordings of Na-montmorillonite-organic complexes. The ratio of total organic material in the system to the amount of clay is shown by the value at the right hand side of each diagram.

The breaks in the curves at about $2\theta=10°$ arise from a change of the intensity scale for the higher order reflections.

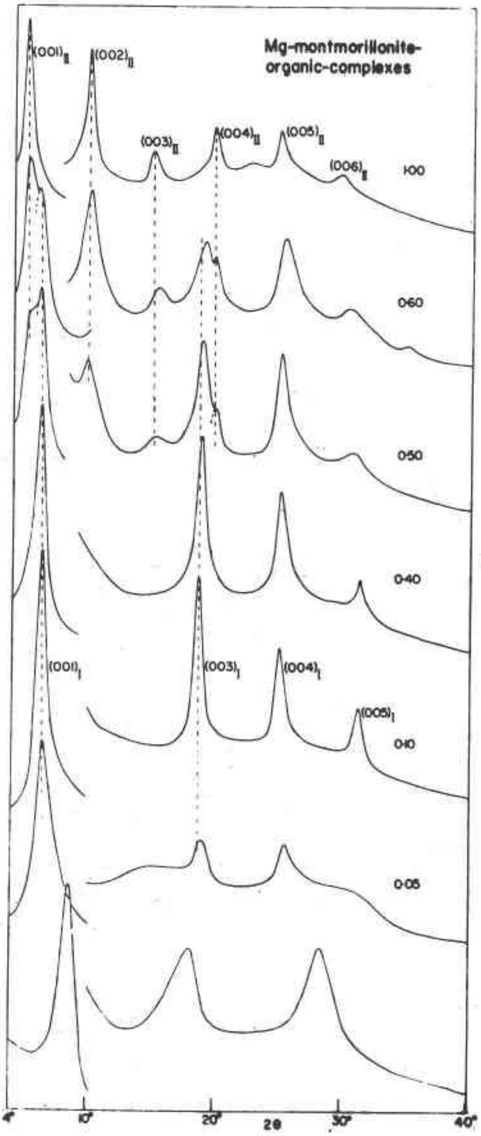


FIG. 4. Diffractometer recordings of Mg-montmorillonite-organic complexes. The ratio of total organic material in the system to the amount of clay is shown by the value at the right hand side of each diagram.

The breaks in the curves at about $2\theta = 10°$ arise from a change of the intensity scale for the higher order reflections.

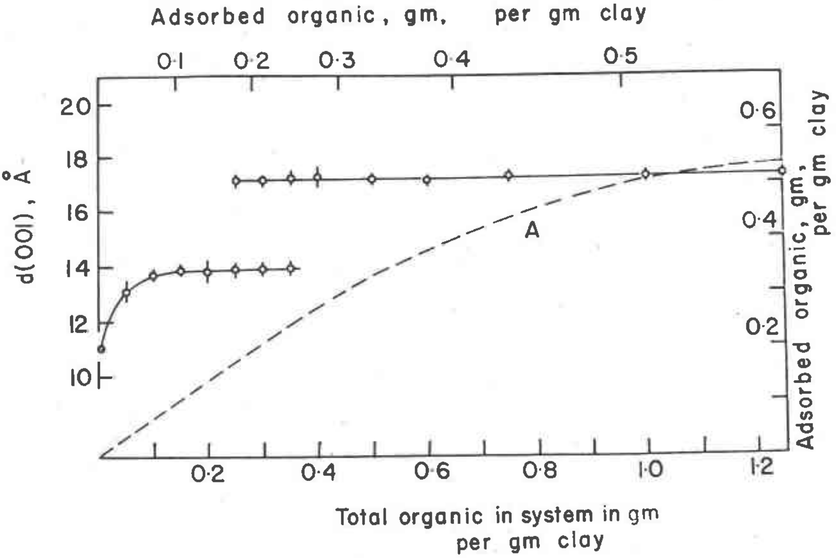


FIG. 5. Lattice spacings in Å of dried Ca-montmorillonite-organic complexes with increasing organic material in the reacting system.
Curve A is the adsorption curve of Fig. 1.

Regularity of a layer structure is indicated by the formation of an integral series of Bragg reflections; the lattice spacing calculated from each reflection with its assumed integral order should then have a constant

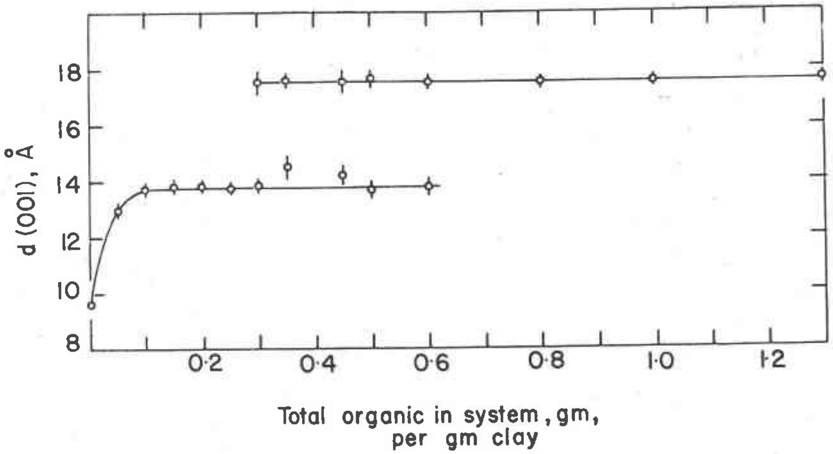


FIG. 6. Lattice spacings in Å of dried Na-montmorillonite-organic complexes with increasing organic material in the reacting system.

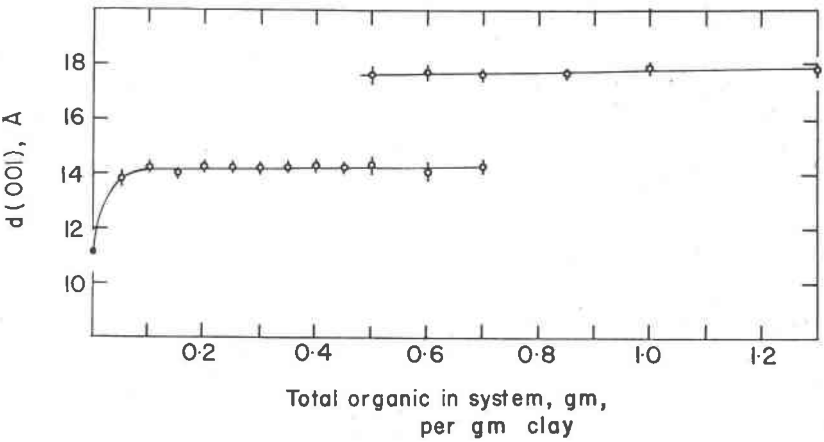


FIG. 7. Lattice spacings in Å of dried Mg-montmorillonite-organic complexes with increasing organic material in the reacting system.

value. Mixed-layer sequences do not give truly integral orders of reflection and if integral orders are assumed, then the lattice spacings derived on this basis do not have a constant value. In Figs. 5, 6, and 7, mean values of *d*(001), obtained from the observed reflections with the assumption of integral orders, are recorded and the short vertical lines indicate the mean deviations of individual values from the average values. The fact that the mean deviations are generally small means that, for the most part, the integral Bragg law is obeyed, i.e., the structures are regular.

Between the composition ranges in which only one basal spacing

TABLE 2. LATTICE SPACINGS, IN Å, OF DRIED FILMS OF MONTMORILLONITE CONTAINING ADSORBED POLYETHYLENE GLYCOL ESTER OF OLEIC ACID (NONISOL 250)

Exchange ion	Fully dried clay	Expanded clays			
		First stage of expansion		Second stage of expansion	
		d	Δd	*d*	Δd
Na	9.6_5	13.8	4.1_5	17.5	7.8_5
Ca	9.7_5	13.9	4.1_5	17.3	7.5_5
Mg	10.0	14.2_5	4.2_5	17.7	7.7
		Mean	4.2_0	Mean	7.7_0

$d(001)$ is recorded, there is a region in which two basal spacings are found simultaneously. This means that in a composition range where irregular interstratified sequences might well have been anticipated, two different ordered phases are found. This is illustrated in Figs. 2, 3, and 4 where reflections arising from structures with one organic layer, and with two organic layers are marked $(00l)_{\mathrm{I}}$ and $(00l)_{\mathrm{II}}$ respectively. It is noticeable in Figs. 5, 6, and 7 that where two basal spacings are found together, the lattice spacings are somewhat less regular than when a single basal spacing occurs.

Between the pure clay end-member and the complex with one organic layer, superpositions of corresponding reflections are not observed, but a progressive shift is found indicating that interstratification of dissimilar layers occurs when the first small amounts of organic material are added to the system. However, the clay lattice expands very quickly to an ordered arrangement with one layer of organic material between the silicate sheets.

(*d*) *X-ray examination of re-wetted clay-organic films*

After examination of the dried films, a few drops of water were placed on each clay-organic film which was then left over-night in a humid atmosphere. Results for the re-wetted films, summarized in Table 1, agree with those for the initial wet films with the one exception that the Na-clay with little organic material did not expand beyond about 19.6 Å.

(*e*) *Stability of the clay-organic films to washing*

The effect of repeated washing of the clay-organic complexes was studied both before and after a drying treatment. After each washing the clay was centrifuged, the liquid removed, fresh water added and a further washing carried out.

The results set out in Table 3 show the dry spacings of Na-, Ca-, and Mg-clays after repeated washings. Two layers of adsorbed organic material can be reduced to one layer, but beyond this stage the organic material could not be removed. A Sohxlett extraction also failed to remove the single adsorbed layer.

DISCUSSION

The similarity of the results for the Na-, Ca- and Mg-clays shows that essentially the same processes are involved in all three clays. However, the adsorption curve, Fig. 1, has been determined only for the Ca-clay. The discussion will therefore be limited to Ca-clay in the first instance. The adsorption curve is superposed on the lattice spacing curves in Figure 4 so that it can be seen at a glance how the swelling of the clay is re-

TABLE 3. LATTICE SPACINGS, IN Å, OF DRIED MONTMORILLONITE-NONISOL COMPLEXES AFTER REPEATED WASHINGS IN WATER

Na-Montmorillonite		Mg-Montmorillonite		Ca-Montmorillonite	
No. of washings	$d(001)$	No. of washings	$d(001)$	No. of washings	$d(001)$
—	17.2 (2-layers)	—	17.8 (2-layers)	—	17.3 (2-layers)
5	13.9 (1-layer)	5	15.5	4	17.2 (2-layers)
		10	13.7 (1-layer)	12	17.2 (2-layers)
		20	13.8 (1-layer)	20	14.0 (1-layer)
—	13.7 (1-layer)	—	14.2 (1-layer)	—	13.8 (1-layer)
5	13.8 (1-layer)	8	14.2 (1-layer)	4	13.9 (1-layer)
10	13.7 (1-layer)	12	13.8 (1-layer)	12	13.9 (1-layer)
15	13.8 (1-layer)	16	13.9 (1-layer)	20	13.8 (1-layer)
				25	13.8 (1-layer)

lated to the adsorbed organic material and to the total organic material in the system.

It has already been noted that there is a marked tendency towards the formation of ordered complexes containing either one layer or two layers of organic material between successive silicate sheets. If P(*n*) denotes a regular phase containing *n* organic layers between successive silicate sheets, and P(*n*,*m*) an irregular sequence in which *n* or *m* organic layers occur randomly between successive silicate sheets, then the sequence of phases observed as the amount of organic material increases in the clay lattice, is as follows:

$$\text{P}(0),\quad \text{P}(0,1),\quad \text{P}(1),\quad \text{P}(1)+\text{P}(2),\quad \text{P}(2).$$

P(0) symbolizes the pure montmorillonite. P(0, 1) appears as an irregular sequence extending from zero to about 0.07 gm. adsorbed organic material per gm. clay which corresponds to about 12% of the saturation value.

The ordered phase P(1) extends from about 0.07–0.17 gm. adsorbed organic per gm. clay, i.e., 12%–30% of the saturated value. The lattice spacing of the P(1) phase is almost constant at 13.9 Å and increases only slightly as the organic content increases. It might be expected that the limit of the P(1) phase would correspond to 50% saturation of the clay. However, when 30% of saturation is reached, some two-layer complex makes its appearance and the mixed phases P(1)+P(2) co-exist in the range 0.17–0.25 gm. adsorbed organic per gm. clay, i.e., 30%–42% of the saturation value.

This symbol, P(1)+P(2), implies that the co-existing phases are regular structures, which is essentially the case, but the regularity is somewhat less perfect than in the single phase ranges. One may therefore picture the P(1) phase as containing a small proportion of two-layer complex and the P(2) phase a small proportion of one-layer complex, but the proportions are too small to make any appreciable change in mean lattice spacing except perhaps in the case of the Na-clay, see Fig. 6.

When the adsorbed organic exceeds 0.25 gm. per gm. clay (42% of saturation), then P(2) alone is formed. This means that even though the organic material is not quite sufficient to fill one layer to maximum capacity, a regular two-layer structure is formed. From 42%–100% saturation, the two-layer complex becomes increasingly filled with organic molecules. Adsorption beyond a two-layer complex does not occur.

In order to visualize how the adsorption complexes are formed, it must be remembered that the adsorption takes place initially when the silicate layers are separated in water. The spacing of the dried films is the result of bringing two adsorbing surfaces together. If each surface had 50% of its maximum adsorption, then it might be expected that the molecules adsorbed on one surface could be accommodated in vacant positions on the adjacent surface, thereby producing one completely filled layer. The results show that for Ca-clay when each surface adsorbs 42% of its maximum capacity, a regular two-layer structure is formed. It must be concluded that the organic molecules are held rather tightly and are not sufficiently mobile to give a close-packed single layer.

The maximum adsorption on each surface to give a single layer P(1) complex occurs at 30% of its maximum adsorptive capacity. When the adsorbed organic content exceeds 30% of saturation, the P(2) complex makes its appearance along with the P(1) complex. It is difficult to explain why some clay particles contain wholly or almost wholly the P(1) complex and others contain wholly or almost wholly the P(2) complex. One is almost forced to conclude that there are minor differences between individual clay particles such that certain particles tend to build up a P(2) complex at a lower organic content than do other clay particles. In consequence, as the organic content in the liquid phase is increased, more and more particles pass over from the P(1) to the P(2) type of complex.

Presumably these differences between particles are not sufficient to influence the initial organic adsorption, for here a mixed-layer phase P(0,1) is produced rather than a mixture of pure montmorillonite P(0), plus a one-layer complex, P(1).

One might hazard a guess that the hypothetical minor differences arise from differences in chemical composition giving rise to different exchange capacities and different layer charges. On this basis it is conceivable that when the organic content in the liquid phase approaches a certain range of values, some particles will be extended to P(2) complexes while others still remain as P(1) complexes.

ACKNOWLEDGMENTS

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