

RANDOM INTERSTRATIFICATION IN ORGANOPHILIC BENTONITES

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ABSTRACT

Organophilic bentonites prepared by reacting various amounts of *n*-laurylamine hydrochloride and dimethyldioctadecyl ammonium chloride with bentonite have been studied by the method of Fourier transforms. The transform curves obtained from the x-ray diffraction patterns of these samples show how different numbers of organic layers between clay laminae are produced by different kinds and amounts of organic material added to the clay. It has been found that as the organic material reacts by base exchange with the clay surfaces, the number of organic layers between each two clay platelets increases in a regular and stepwise manner.

INTRODUCTION

Random interstratification in the clay minerals has been of interest for many years. A study of the stacking characteristics of the various clay minerals either within a single species or mixed systems, such as montmorillonite-chlorite, montmorillonite-vermiculite, etc., has led to an increased knowledge as to the structures and behavior of the clay minerals.

Various methods of studying interstratification in the clays have been developed. These, in general, are based on methods of interpretation of the x-ray diffraction patterns of the various clays such as the procedures of Hendricks and Teller (1942), Méring (1949), and MacEwan (1953). Other methods such as that of Weiss and Rowland (1956) are based on a special means of obtaining the x-ray diffraction patterns, such as heating, so as to be able to distinguish the different types of clay layers that may be present in a given sample.

A previous paper (McAtee, 1956) showed how random interstratification in montmorillonite was studied by means of the Fourier transform method of MacEwan (1953). The degree and type of random interstratification within mixed calcium and sodium montmorillonites were effectively studied by this method. This paper extends the study to random interstratification within montmorillonites which have been reacted by means of a base exchange reaction with various amines and quaternary ammonium compounds.

MATERIALS AND EXPERIMENTAL METHODS

The organophilic bentonites were prepared from centrifuged Wyoming bentonite of the Colony, Wyoming, area and amine salts and quaternary ammo-

nium salts. The specific organic compounds of bentonite that were prepared for this study were the following: *n*-laurylamine bentonite and dimethyldioctadecyl ammonium bentonite.

The samples were prepared by centrifuging a 3 percent dispersion of Wyoming bentonite with either a Sharples Super Centrifuge or a Merco type C-9 Continuous Centrifuge. The centrifuged slurry was then heated to 60-70°C and, while agitating, the amine salt or quaternary ammonium salt was slowly added. The flocculated clay complex was then washed by filtering and repulping for removal of soluble salts. It was then filtered and dried in an air-circulating oven at 65°C and pulverized in a laboratory hammer mill.

Samples for x-ray diffraction examination were prepared by a procedure which would yield diffraction data of only the basal spacings: The different organophilic bentonites were first dispersed in a suitable organic liquid such as acetone, toluene, methylethyl ketone, or acetone with benzene. Each different bentonite required a study to determine the organic liquid that was the most effective in obtaining maximum dispersion and orientation. After the dispersion of the treated clay in the organic liquid was complete, several drops of the material were placed on a glass microscope slide and allowed to dry at room temperature. Several of the samples were also dried at elevated temperature in order to be sure that all of the organic liquid used as the dispersant was being evaporated. The x-ray diffraction patterns of the oriented samples were obtained with a North American Philips High Angle Spectrometer using Ni filtered $\text{CuK}\alpha$ x-radiation.

EXPERIMENTAL RESULTS AND DISCUSSION

The Fourier transform equation employed in these calculations was that published by MacEwan (1953). The transform as used can be written as follows:

$$T(R) \approx \sum_R \frac{I_R}{\Theta |F_l|^2} \cos 2\pi\mu_R R$$

This cosine transform is essentially the Patterson line projection on the *c*-axis of the crystallites. Its values are proportional to the mean number of layers at a distance *R* from any arbitrary layer chosen as the origin. This form of function gives a peak at the origin and the terms are as follows: I_R is the observed intensity for each value of reciprocal spacing μ . F_l is the structure factor of a single layer and θ is the Lorentz-polarization factor.

The factor F_l which appears in the denominator of the transform equation is the structure factor of a single layer of clay complex. The use of this term requires the assumption that all the layers are the same and the scattering by the interlamellar material is small. The first part of this assumption cannot be fulfilled because the very nature of the calculations is to determine the components of a mixture. However, it has been found by trial and error that the effect of different layers on F_l is small, so this effect can be ignored.

The second assumption, that the scattering of x-rays is small by the interlamellar material, is not negligible in the case of the organo-treated clays. In a previous paper (McAtee, 1956) on the Fourier transform study of sodium-calcium montmorillonite, it was found that the interlamellar water did not cause a great amount of scattering; therefore, its effect could be ignored in the calculations. The organic interlamellar material, however, does cause scattering and can not be disregarded from the calculations of F_l . In order to correct this condition, it was found that new F_l curves had to be constructed. A family of $|F_l|^2$ vs. $\sin \theta/\lambda$ were constructed for different numbers of layers of $(\text{CH}_2)_n$ chains between the montmorillonite platelets.

The structure factor of the theoretical one-half unit cell of montmorillonite may be written:

$$(1) \quad F_l = W + X + Y + Z$$

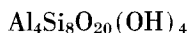
where $W = 2 f_{\text{Al}} \cos 0^\circ$
 $X = 4 f_{\text{Si}} \cos 2 \pi (2.7/x)$
 $Y = 6 f_{\text{O}} \cos 2 \pi (1.1/x)$
 $Z = 6 f_{\text{O}} \cos 2 \pi (3.3/x)$

where $x = \text{Al}$ to Al plane distance, and varies for the calculations made from $\sin \theta/\lambda = 0$ to $\sin \theta/\lambda = 0.20$ or from $\infty \text{ \AA}$ to 2.5 \AA . The term f is the atomic structure factor for the atom noted.

Corrected $|F_l|^2$ values for the organophilic bentonites were obtained by use of the following equations:

- (2) For 1 layer of organic per one-half unit cell.
 $F_l' = F_l + 3.4 f_{\text{C}} \cos 2 \pi (6.6/x)$
- (3) For 2 layers of organic per one-half unit cell.
 $F_l'' = F_l + 7.5 f_{\text{C}} \cos 2 \pi (6.6/x)$
- (4) For 3 layers of organic per one-half unit cell.
 $F_l''' = F_l'' + 3.4 f_{\text{C}} \cos 2 \pi (10.6/x)$
- (5) For 4 layers of organic per one-half unit cell.
 $F_l'''' = F_l''' + 7.5 f_{\text{C}} \cos 2 \pi (10.6/x)$

The values 3.4 and 7.5 were obtained from a consideration of the number of (CH_2) groups that can be placed on a surface area of a half unit cell of montmorillonite. The theoretical formula for montmorillonite is



with a net negative charge of 0.33 units per half unit cell.

Jordan (1949) has shown that an addition of 100 meq of a 10 carbon amine to bentonite gave a single-layer type complex. It was reasoned that for this type, the organic molecules on the top surface of one lamina fit into the gaps between those on the bottom surface of the lamina directly above it; therefore, each amine chain can occupy no more than 50 percent of the available surface area per plate surface. It was calculated that a 10 carbon atom amine coated 49 percent of the clay surface area. Since each half unit cell of montmorillonite has a net charge or exchange capacity of 0.33 units, then:

$$\frac{0.33 \times 10 \text{ C atoms}}{0.49 \times 2} = 3.4 \text{ C atoms per one-half unit cell.}$$

The value of 7.5 can be calculated in a similar manner from data for an 18 carbon atom amine-bentonite. This forms a two layer complex; therefore, each surface of clay can be completely covered by the organic molecule. Jordan (1949) has shown that the area covered by this amine is 79 percent; therefore:

$$\frac{0.33 \times 18 \text{ C atoms}}{0.79} = 7.5 \text{ C atoms per one-half unit cell.}$$

The values of 6.6 and 10.4 which appear in equations 2 to 5 are the distance that the $(\text{CH}_2)_n$ chains are found from the Al layer. The values were obtained from one-dimensional Fourier series of regular clay-organic complexes such as that published by Bradley (1945).

The corrected $|F_l|^2$ curves of 1, 2, 3, and 4 layers of $(\text{CH}_2)_n$ groups are shown in Figure 1. The d -spacing noted with each curve represents the basal spacing of a particular type of organophilic bentonite that satisfies a given curve. For each diffraction line, the value of $\sin \theta/\lambda$ was determined and the corresponding $|F_l|^2$ curve was read from the correct curve shown in Figure 1.

Laurylamine Bentonite

A series of n -laurylamine bentonites was prepared for Fourier transform determinations. This series consisted of six samples containing the following milliequivalents of amine/100 g bentonite: 61, 71, 85, 99, 106, and 117. This represents organophilic bentonite from a 1-layer type through a transition zone to a 2-layer type. The x-ray line diagrams of the oriented n -laurylamine bentonites are shown in Figure 2. The lower set of lines shows the positions for the basal spacings of theoretical 1-layer and 2-layer organo-bentonites.

It can be seen from Figure 2 that the 13.5Å (001) spacing of the n -laurylamine bentonite (1-layer organo-bentonite) remains fairly constant through the 85 meq sample and that the higher orders are integral. Above 85 meq, there is a shifting of the basal spacing to 17.6Å with corresponding sets of nonintegral higher orders. The samples with x-ray patterns in the transition region are the most interesting from a Fourier transform standpoint since this is the region of mixed layering of 1- and 2-layer type organo-bentonites.

Figure 3 shows the Fourier transform curves for several of the samples, namely the 61, 85, 106, and 117 meq samples. The transform curve for the 61 meq sample is a simple repeat-type curve which is representative of a uniform sample with no interstratification. Between each two platelets there is one layer of organic $(\text{CH}_2)_n$ chains.

The 85 meq curve is starting to show some interstratification effects. There is a general broadening of the peaks, and there is some indication of the appearance of a combination peak such as the AB type. (AB type means a combination of a 1-layer with a 2-layer type organo-bentonite.)

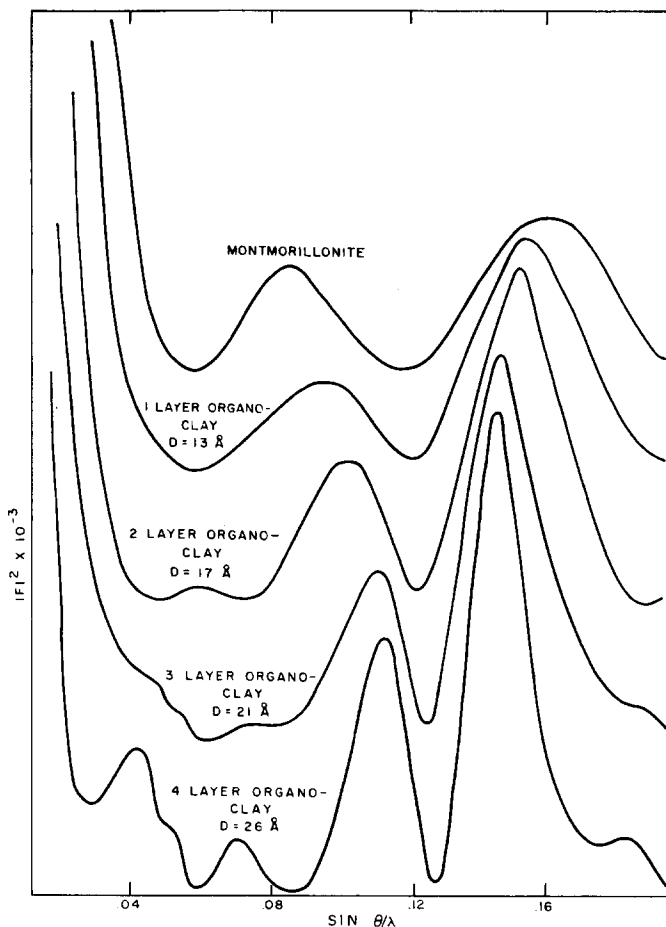


FIGURE 1. Structure factor curves for 1, 2, 3, and 4 layer organophilic bentonite.

The relative intensities of the peaks for an individual transform curve represent the ratio of the different types of material present in the sample. Using this as a guide, it will be noted that as the meq of amine/100 g clay is increased to 106 meq and then to 117 meq, the amount of 2-layer type (peaks noted as *B*) increases. The combination type *AB* increases to a maximum at 106 meq and then starts to decrease with the 117 meq sample.

The clay platelets are initially separated by one layer of amine. As more than 50 percent of the surface of adjacent flakes becomes covered, crowding takes place and the flakes become separated by two layers of amine. Apparently the 2-layer type appears in a random manner so that the *AB* or alternating type material reaches a maximum. As the amount of amine is increased to

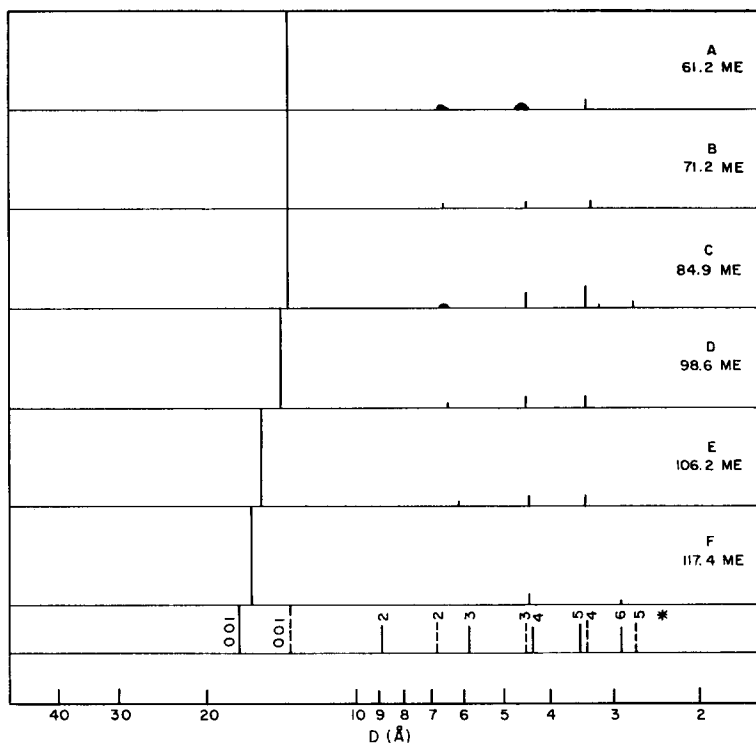


FIGURE 2.—X-ray diffraction diagrams for *n*-laurylamine bentonite. *Dash line: Theoretical basal spacing for 1 layer organo-clay. Full line: Theoretical basal spacing for 2 layer organo-clay.

117 meq/100 g clay, groups of two layers of *B* type start to predominate, as shown by the relative intensity of the transform peak.

Dimethyldioctadecyl Ammonium Bentonite

A series of dimethyldioctadecyl ammonium bentonite was prepared and examined by x-ray diffraction. The amount of dimethyldioctadecyl ammonium chloride that was added to the centrifuged bentonite was as follows: 91, 95, 99, 102, 105, 112, 118, and 129 meq/100 g clay.

The base-exchange capacity of the bentonite used for the preparation of these samples was 95 meq/100 g clay. It is apparent therefore, that all but the first two of these samples have an amount of quaternary compound greater than the exchange capacity. The x-ray diffraction patterns (Fig. 4) show that the samples have basal spacings ranging from 22Å to as high as 35Å.

Fourier transforms for several of these samples are shown in Figure 5. The sample containing 91 meq of quaternary compound gave a basal spacing of 22Å. The corresponding Fourier transform indicates that this is primarily a

3-layer type (theoretical 001 value is 21.5A) with small amounts of 2-layer and 4-layer material. The next transform peak is at 44A or the second order stacking of the 22A peak.

As the amount of quaternary compound is increased, the x-ray pattern shows a change of the basal spacing through 24A (95 and 99 meq of organic/100 g clay) and then to 26A for the 105 and 112 meq of organic samples. The Fourier transform for the sample containing 95 meq of organic is shown in Figure 5. This is primarily a mixture of 3- and 4-layer material and the amount of 4-layer material predominates.

The next transform curve shown in Figure 5 is for the sample containing 102 meq of dimethyldioctadecyl ammonium ion. There is a shoulder at 30A

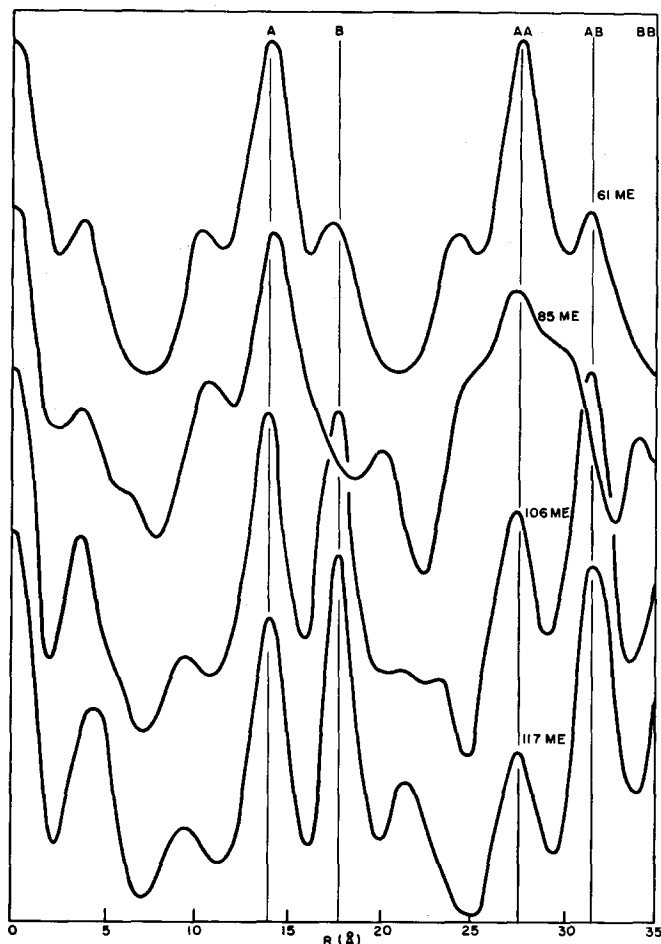


FIGURE 3. — Fourier transform curves for *n*-laurylamine bentonite.

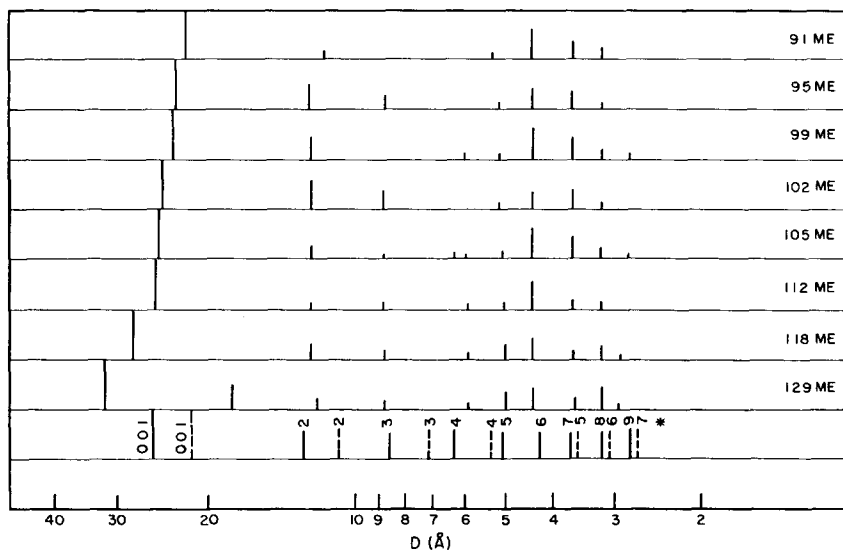


FIGURE 4.—X-ray diffraction diagrams for dimethyldioctadecyl ammonium bentonite. *Dash line: Theoretical basal spacing for 3 layer organo-clay. Full line: Theoretical basal spacing for 4 layer organo-clay.

which corresponds to a 5-layer type, and a peak has developed at 35Å (or a 6-layer type organophilic bentonite). The peak near 42Å is a second order of 21Å or the 3-layer peak.

The samples that gave 26Å basal spacings gave integral higher orders; therefore, the Fourier transform would show only a regular 4-layer type organophilic bentonite.

As the amount of organic was increased to 118 meq of organic/100 g clay, the basal spacing increased to 28Å and the Fourier transform curve showed an increase in the amount of 5- and 6-layer type material. From the relative intensities of the transform peaks for the 118 meq and the 102 meq samples, it would appear that the 6-layer type material forms a more stable configuration than does the 5-layer type.

The final curve shown in Figure 5 is for a sample containing 129 meq of dimethyldioctadecyl ammonium ion/100 g clay. The basal spacing for this sample is 35Å. The Fourier transform curve shows that this sample consists almost entirely of 6 layers of organic material between each two clay platelets.

The two series of organophilic bentonites that have been discussed here represent a wide range of samples. They go from a relatively short chain type primary amine forming 1- to 2-layer type complexes to a massive long chain quaternary forming up to 6 layers of organic between each two clay platelets. The general conclusions from this study are that the clay tends to add the organic material in a fairly regular and orderly fashion. The short chain type organophilic bentonite tends first to show interstratification effects as the

appearance of combination peaks on the Fourier transform curve. This indicates that as the amount of amine is increased to a point above 50 percent coverage of the clay platelet surface, crowding takes place and a second layer of amine enters into a portion of the system. From the changes of the relative intensities of the Fourier peaks, it is reasoned that the second layer of organic which forms between each set of platelets tends to go to completion before the third or next successive layer of amine starts separating the platelets. Because of this, the amount of *AB*-type material (Fig. 3) increases to a maximum and then starts to decrease as the amount of *B* (2 layer) material increases above the *A* (1 layer) type of complex.

Upon the addition of a larger, longer chain type amine such as the dimethyl-

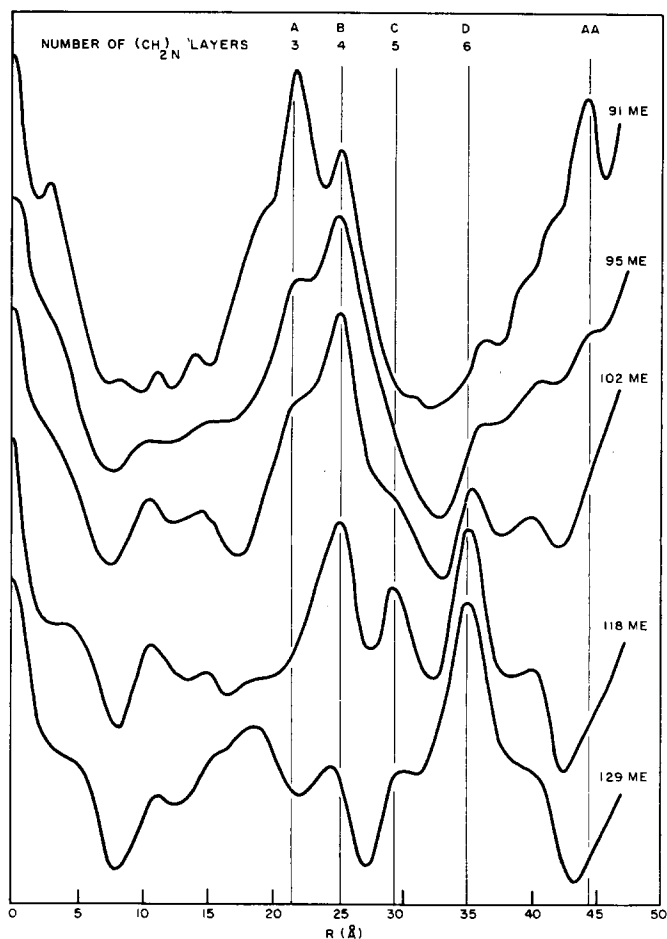


FIGURE 5.—Fourier transform curves for dimethyldioctadecyl bentonite.

dioctadecyl ammonium chloride to bentonite, a 4-layer type system develops as saturation of the exchangeable positions with organic takes place. The hydrocarbon chains have to overlap the tops of the chains adjacent to the clay surface. This type of stacking apparently can continue to at least three layers per clay surface or a total of six layers between each two clay laminae. The sample which showed the maximum of this effect had 129 meq of organic/100 g clay, which is some 34 meq above the B.E.C. of the clay. This extra 34 meq of quaternary compound is not reacted with the clay by base exchange but is adsorbed on the surface of the clay. Apparently the adsorbed quaternary compound tends to enter between two plates and becomes adsorbed on the adjacent surfaces in somewhat equal amounts. Therefore, the system tends to go directly from a 4-layer complex to a 6-layer complex with very little 5-layer material being formed.

The Fourier transform study of these organophilic bentonites has resulted in a better understanding of the way different types of organic material and increasing amounts of these materials complex with bentonite surfaces. It would appear that the clay tends to complex the organic in a fairly regular and stepwise manner. As organic is added to the system up to the B.E.C. of the clay, more and more platelets become separated by one more unit layer until all the platelets are separated by an equal number of layers. Above the B.E.C. of the clay, adsorption of the organic takes place on both surfaces of adjacent flakes simultaneously so as to increase the spacing by units of two layers at a time.

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REFERENCES

- Bradley, W. F., 1945, Molecular associations between montmorillonite and some polyfunctional organic liquids: *J. Amer. Chem. Soc.*, v. 67, p. 975-981.
- Hendricks, S. B., and Teller, E., 1942, X-ray interference in partially ordered layer lattices: *J. Chem. Phys.*, v. 10, p. 147-167.
- Jordan, J. W., 1949, Organophilic bentonites. I. Swelling in organic liquids: *J. Phys. and Colloid Chem.*, v. 53, p. 294-306.
- MacEwan, D. M. C., 1953, Randomly stacked layers in clay minerals: *Nature*, v. 171, p. 616-617.
- McAtee, J. L., 1956, Determination of random interstratification in montmorillonite: *Amer. Min.*, v. 41, p. 627-631.
- Méring, J., 1949, The scattering of x-rays by systems of disordered stratification: *Acta Cryst.*, v. 2, p. 371-377.
- Weiss, E. J., and Rowland, R. A., 1956, Oscillating-heating x-ray diffractometer studies of clay mineral dehydroxylation: *Amer. Min.*, v. 41, p. 117-126.