

EXPERIMENTAL STRUCTURE FACTOR CURVES OF MONTMORILLONITES

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ABSTRACT

Diffraction from oriented flakes of four montmorillonites that had been treated with an excess of four glycols was obtained. Peak areas for the $00l$ diffraction from each of the treated clays were plotted against $\sin \theta/\lambda$.

It was assumed that the observed diffraction intensity for the complexes was equal to that of the clay plus or minus that of the organic part of the complex. By assuming also that the contribution from the organic part of the complex is the same for each clay at any one value of $\sin \theta/\lambda$, a systematic consideration of all the possible levels of contribution by the organic interlayer material could be made. At values of $\sin \theta/\lambda$ where intensity data were closely spaced, it was found that only one of the possible levels of contribution by the organic interlayer material would allow a residual intensity (attributable to the clay) that fit on smooth curves.

Curves of the diffraction intensity attributable to each of the clays resembled, in their gross features, the calculated structure factor curve of mica. Displacements of the nodes along the $\sin \theta/\lambda$ axis and differences in loop heights are sufficient to make this experimental structure factor curve for each of the five clays quite distinctive.

INTRODUCTION

X-ray diffraction analysis offers two easily measurable quantities, the angle and intensity of diffraction. Both of these quantities are highly variable for materials that are called montmorillonites. Variations in the diffraction angle have been related to hydration level and sample composition (dioctahedral or trioctahedral) to the extent that they can be used analytically, but intensity variations have received less attention.

The organization of intensity variation data was first attempted by comparing single line intensities with theoretical intensities from structure factor calculations based on the three-layer model for montmorillonite. A great improvement over this procedure was made by Bradley (1953), who produced an experimental curve showing intensity as a continuous function of the diffraction angle for montmorillonite. This curve was a composite of many intensity measurements from $00l$ lines of powder patterns of organic-clay complexes. Bradley's curve differs somewhat from the corrected structure factor curve based on what is accepted as the montmorillonite model.

More progress in the interpretation of intensity variation of montmorillonite requires that curves similar to Bradley's be produced for individual montmorillonite samples and then compared. Curves of this kind could be expected to serve as a means of differentiating among the large group of minerals now called montmorillonite but known to differ in their physical properties. The

curves would make possible a better interpretation of these differences through comparison with calculated structure factor curves of several different models.

Many factors enter into determining diffraction intensity besides the structure factor. A complete expression of diffracted intensity is difficult to state. Some of the controlling factors are

$$I = I_0 p V A T O |F|^2 \text{ (function of } \theta \text{)} \quad (1)$$

where I = diffracted intensity

I_0 = incident beam intensity

p = multiplicity factor

V = volume of sample irradiated

A = absorption factor

T = temperature factor

O = orientation factor

F = structure factor

θ = diffraction angle.

Ideally, all these factors should be determined so that a direct comparison between measured and calculated intensities could be made with validity. On the other hand, the necessity of evaluating all the intensity-determining factors can be avoided by limiting the comparison to changes in structure factor and changes in intensity. If this type of analysis is used, the data-gathering procedure must be carefully standardized in order to make all the intensity-determining factors constant except the structure factor.

Accordingly, the discussion of the data presented in this paper will deal entirely with relative intensities and their qualitative comparisons with calculated structure factors. Except for the uncertainties that will be discussed later, the relation

$$I \propto F^2 \quad (2)$$

will be adequate for the interpretation of intensity curves.

THEORY

The basic general geometrical structure factor formula given by James (1948, p. 31) is

$$F_{hkl} = \sum_j f_j e^{-2\pi i(hu_j + kv_j + lw_j)}$$

When considering only 00 l diffraction from a crystal with a plane of symmetry parallel to (00 l), the relation is simplified to

$$F_{00l} = \sum |f_j| \cos 2\pi lw_j$$

where w_j is the coordinate of each atom layer parallel to (001) and l is the order of the diffraction. Figure 1 shows the variation of the $\cos 2\pi lw_j$ term with $\sin \theta/\lambda$ for each of the atom layers in the mica structure using the octahedral cation layer as the origin. The structure factor at any $\sin \theta/\lambda$ is equal

to the algebraic sum of each of these cosine functions individually multiplied by the atomic scattering factor, $|f_j|$, of the material composing that layer in the crystal. These are continuously summed to produce the curve in the lower part of Figure 1 for a sodium-aluminum mica.

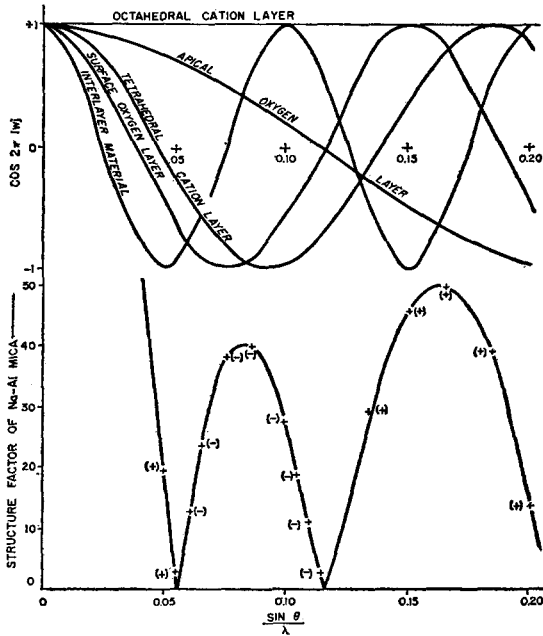


FIGURE 1. — Variation of $\cos 2\pi l w_j$ with $\sin \theta / \lambda$ for each of the atomic layers of the mica structure (top) and the summation for a sodium-aluminum mica (bottom).

The value of the structure factor at $\sin \theta / \lambda$ from zero to 0.03 is highly positive because all the layers contribute to a positive sum. Any diffraction line appearing in this region will be expected to be very intense. From 0.03 to 0.05, contributions from the interlayer material, the surface oxygens, and the tetrahedral cations all become negative. At about 0.06 the negative contributions balance the positive ones from the apical oxygen and octahedral cation layers, giving the structure factor a low value. Diffraction occurring near this value of $\sin \theta / \lambda$ will be expected to have a low intensity.

Similar reasoning can show that diffraction occurring near $\sin \theta / \lambda = 0.11$ will have a low intensity because of the low structure factor resulting from the balance of negative contributions from both the surface oxygen layer and the tetrahedral cation layer, and positive contributions from interlayer material and the octahedral cation layer. The cosine function of the apical oxygen layer is near zero. In the sodium-aluminum mica calculation the negative tetrahedral cation layer and the layer of surface oxygens have the larger $|f_j| \cos 2\pi l w_j$ sum resulting in a negative structure factor.

Likewise, the positive loop of the structure factor curve centered around $\sin \theta/\lambda = 0.15$ is a balance of negative contributions from the interlayer material in addition to that from the apical oxygens, and positive contributions from the surface oxygen layer, tetrahedral cation layer, and octahedral cation layer. The positive $|f_j| \cos 2 \pi l w_j$ sums are greater in the mica calculation, resulting in a positive structure factor in this region.

An increase in the quantity of scattering material in the octahedral cation layer, for example, substituting iron for the aluminum, will tend to decrease the structure factor and therefore the intensity of lines occurring near $\sin \theta/\lambda = 0.09$ and at the same time increase the structure factor and the intensity of lines occurring near $\sin \theta/\lambda = 0.15$. Decreasing the quantity of scattering material in this part of the crystal will have the opposite effect on line intensities.

Decreasing the scattering ability of the crystal in the tetrahedral cation layer by substitution of an aluminum for silicon, or a silicon omission, would tend to decrease intensities in both the 0.09 and 0.15 regions where this position in the crystal contributes to the dominant sum.

Diffraction collected from the (00*l*) series of organic-montmorillonite complexes has an intensity related to the sum of all the contributions from the silicate layer plus that from the organic molecules which have been shown by Bradley (1945) to form a layer about 7Å removed from the octahedral layer reference. Figure 2 (top) is a plot of the variation of $\cos 2 \pi l w_j$ for the several layers of scattering material in a montmorillonite-organic complex. Figure 2 (bottom) is a summation of contributions from the silicate part of an aluminum montmorillonite shown as a solid line. The modification to be expected by the introduction of organic molecules in a layer at 7Å is shown as a dashed line. The amplitude of the negative loop from 0.05 to 0.11 is reduced and displaced away from the origin. The second loop from 0.11 to 0.20 is increased in amplitude and its maximum is shifted toward the origin.

Diffraction data from several organic complexes with different periodicities for one montmorillonite would be expected to give an erratic curve of intensity versus $\sin \theta/\lambda$ because the intensities represent diffraction from essentially different materials. Each organic liquid contributes differently to the total intensity. Figure 3 shows data of this kind plotted. If an appropriate contribution to the total intensity from each of the interlayer organic materials could be subtracted from the total intensity, the remainder would be diffraction from a common material, the silicate part of the complex. The intensity data plotted as in Figure 3 have been adjusted to produce a smooth curve which is to be expected for montmorillonites. This adjustment would be far from unique, and the chance of making the proper adjustment for each organic interlayer contribution would be small. It would, therefore, be difficult to arrive at a truly characteristic intensity curve for the montmorillonite.

Whatever the appropriate contribution of an organic interlayer material to the diffraction intensity of a complex is, it should be the same for complexes of that organic liquid with all montmorillonites, provided all the complexed

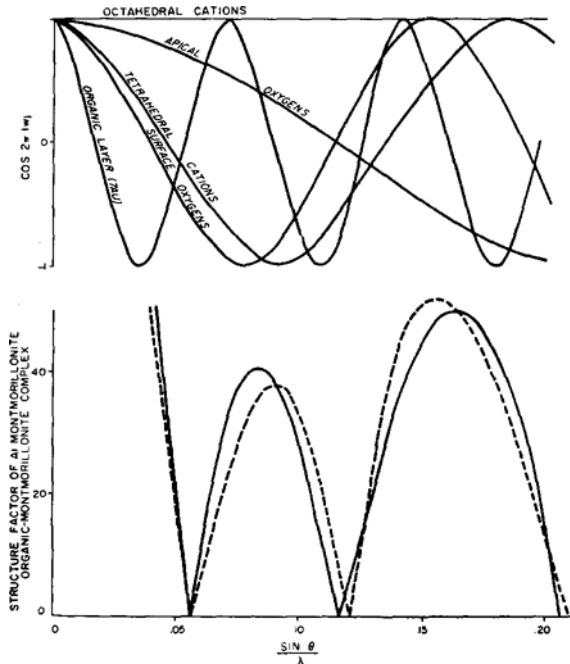


FIGURE 2.—Variation of $\cos 2\pi l w_j$ with $\sin \theta/\lambda$ for each of the atomic layers of an organic-montmorillonite complex (top) and the summation (bottom) of the silicate part of the structure (solid line) with the modification caused by the interlayer organic material (dashed line).

montmorillonites had the same basal periodicity. If intensities from complexes of two montmorillonite samples with the same organic liquid are compared line for line, the differences would be attributable to differences in the silicate part of the complex. Equal adjustment of comparable lines from the complexes of the two montmorillonite samples could be made so as to produce smooth intensity curves for both of the montmorillonite samples. Comparison of intensity data from the two complexed montmorillonites reduces the choice of adjustments of the raw data that can be made to produce two smooth curves. The dependability of the adjustment is likewise increased. As the number of complexed montmorillonite samples to be considered is increased, the more nearly unique is the determination of the contribution of the organic interlayer material. The intensity curve derived in this way for each montmorillonite correspondingly becomes more characteristic as the number of montmorillonites considered increases.

EXPERIMENTAL PROCEDURE

Intensity curves of montmorillonite are produced from diffraction data of several organic-clay complexes that must be individually prepared and still

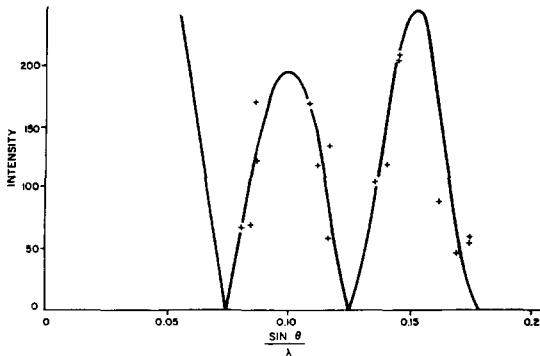


FIGURE 3.—Intensity data for complexes of Wyoming Bentonite I before adjustment.

validly compared. Every step in the sample preparation must be examined meticulously for its possible effect on the intensity of the diffraction lines. The relation between diffraction intensity and some of its controlling factors has already been stated. These variables can be divided into categories such as instrumental variables, sample variables, and personal variables.

The principal approach to instrumental variable standardization was to take all the data as rapidly as possible to minimize effects of aging of the apparatus or possible recalibration. The preset control feature of the General Electric XRD-3 made possible reasonable reliance on the reproducibility of incident x-ray intensity, I_0 , of Equation 1. Spectrometer traces were all made with identical settings of the detector variables. Measurements of the areas under the spectrometer trace peaks were used as intensities. No attempt to scale the diffraction maxima was made, although this procedure will be used to collect future data. At the present stage of the investigation it was not felt necessary to account strictly either for accurate intensity or for the nonadditivity of intensities while appraising features additive as amplitudes.

The sample preparation was designed to insure uniformity of the geometrical characteristics of samples, the degree of preferred orientation, and the degree of solvation of the montmorillonites. The use of oriented flakes simplified the spectrometer traces and minimized the possible distortion or intensity modification of any of the $00l$ lines by diffraction from another set, thus standardizing the multiplicity factor, p , of Equation 1. One disadvantage in using oriented flakes is the uncertainty that all the samples will produce flakes having the same degree of orientation. Failure to produce comparable degrees of orientation in the flakes of two samples would only result in all the diffraction from the well-oriented sample being more intense than that from the less well oriented. The value of O in Equation 1 would be changed. If the flakes of a single sample were of uniform orientation, a smooth intensity curve characteristic of that clay should be obtainable from the data. The amplitudes of all of the peaks on the intensity curve would be uniformly changed by a change in the degree of orientation. Because the value of O is not known to be

uniform for the flakes of all montmorillonites that were used, the interpretation of intensity curves must depend more on relative peak heights of the curve from one sample rather than on a direct comparison of the curves from two samples.

Flakes were prepared from suspensions of particles that were less than two microns equivalent spherical diameter. All suspensions were adjusted to the same concentration. The flakes were prepared by allowing equal volumes of the suspensions to dry slowly on microscope slides. This procedure insured uniformity of weight of sample per unit area of the flakes. If the clays were not greatly different in specific gravity, the flakes would be of uniform thickness, and the value of V in Equation 1 would be standard. The absorption properties of the clays almost certainly differ, making A variable. Any difference would increase the amplitude of all the peaks on the intensity curve of a mineral with low absorption. This still allows a smooth intensity curve that is characteristic of the clay to be derived from the data, but it prohibits direct comparison of curves of two clays.

The flake area was larger than the incident beam spot on the sample at the lowest angle at which diffraction was registered. The useful sample area was determined, therefore, by the collimation angle of the incident beam.

Organic liquids that were used in this study were all polyhydroxy alcohols which form a type of complex with montmorillonite that is similar to that with water. Only complexes that were stable under atmospheric conditions for a period of 24 hours were used. Any montmorillonite sample that showed signs of developing two solvation levels during this time was discarded. The organic liquid was spread on the surface of the flake and replenished periodically so that there was always an excess.

Finally, all the above sample preparation work was done by one man, Thomas E. Brown, in an effort to minimize the effects of any personal errors.

DATA AND RESULTS

Table 1 shows the raw intensity data for organic complexes of four montmorillonite samples. These raw data are plotted in Figure 3 for Wyoming Bentonite I. In the second column under each sample, the adjustments are listed that were used to bring all the intensities onto smooth curves for the four samples. This adjustment is that portion of the total diffraction intensity that is attributable to the interlayer organic material. The same adjustment was used for comparable lines of all four montmorillonite samples.

Table 2 shows an arrangement of the adjustments for each organic complex. The cosine functions of the structure factor for the 7A position at the values of $\sin \theta/\lambda$ where the adjustments are made are listed in the second column. This cosine function multiplied by the scattering factor, f , for the organic interlayer material should be directly comparable with the interlayer contribution or adjustment. The value of f is not known, but it is a continuously diminishing function of $\sin \theta/\lambda$. The major fluctuations in the adjustments therefore should be caused by the cosine function. Comparison of the cosine function

TABLE I. — DIFFRACTION INTENSITIES OF MONTMORILLONITE-ORGANIC COMPLEXES

Organic Liquid	Order of Diffraction	Hectorite		Wyoming Bentonite I		Wyoming Bentonite II		Wyoming Bentonite III		Sin θ λ			
		Complex	Organic	Complex	Organic	Complex	Organic	Complex	Organic				
B	3	50	- 10	40	70	- 10	60	18	- 10	27	- 10	17	.081
B	4	72	+150	222	170	+150	320	35	+150	35	+150	185	.108
B	5	150	+ 20	170	105	+ 20	125	18	+ 20	25	+ 20	45	.135
B	6	117	+150	267	90	+150	240	28	+150	42	+150	192	.162
C	3	143	- 55	88	123	- 55	68	60	- 55	35	- 55	20	.087
C	4	25	- 5	20	35	- 5	30	11	- 5	18	- 5	13	.116
C	5	390	+ 40	430	210	+ 40	250	80	+ 40	57	+ 40	97	.145
C	6	50	0	50	59	0	59	24	0	15	0	15	.174
D	3	220	-110	110	161	-110	51	130	-110	143	-110	33	.087
D	4	45	- 40	5	60	- 40	20	33	- 40	48	- 40	8	.116
D	5	450	0	450	209	0	209	128	0	140	0	140	.145
D	6	112	- 35	77	60	- 35	25	48	- 35	38	- 35	3	.174
E	3	121	- 30	91	72	- 30	42	45	- 30	54	- 30	24	.084
E	4	308	- 65	243	117	- 65	52	90	- 65	112	- 65	47	.112
E	5	429	- 30	399	120	- 30	90	90	- 30	120	- 30	90	.140
E	6	216	0	216	48	0	48	36	0	56	0	56	.168

B = Propylene glycol complex
 C = Ethylene glycol complex
 D = Diethylene glycol monoethyl ether complex
 E = Glycerol

TABLE 2. — INTENSITY CONTRIBUTIONS FROM INTERLAYER MATERIAL

	$\frac{\sin \theta}{\lambda}$	Adjustment	$\cos 2 \pi l w_j$ for the 7AU Position
Propylene Glycol			
Third order	0.081	10	+ .66
Fourth order	0.108	150	- .99
Fifth order	0.135	20	+ .76
Sixth order	0.162	150	- .06
Ethylene Glycol			
Third order	0.087	55	+ .18
Fourth order	0.116	5	- .70
Fifth order	0.145	40	+ .98
Sixth order	0.174	0	- .90
Diethylene Glycol- Monoethyl Ether			
Third order	0.087	110	+ .18
Fourth order	0.116	40	- .70
Fifth order	0.145	0	+ .98
Sixth order	0.174	35	- .90
Glycerol			
Third order	0.084	30	+ .44
Fourth order	0.112	65	- .90
Fifth order	0.140	30	+ .97
Sixth order	0.168	0	- .57

for 7A with the adjustment shows that not even a qualitative relation exists. This lack of correlation suggests that there is an intensity-determining factor which has not been duplicated from one complex to the next or that the uncorrelatable adjustments may include factors other than the interlayer organic contribution to diffraction intensity.

The adjusted diffraction intensities have been plotted against $\sin \theta/\lambda$ for the four montmorillonites in Figures 4, 5, 6, and 7. Values of $\sin \theta/\lambda$ where 001 diffraction occurs for the four organic complexing agents that were used are marked by solid vertical lines. The estimated portions of the curves where intensity data are widely spaced are dashed. Data from additional complexes are being added now to fill in these uncertain parts of the curves.

Figure 4 of hectorite, a well-known trioctahedral magnesium montmorillonite, shows intense diffraction near $\sin \theta/\lambda = 0.15$ and relatively weak diffraction near 0.09. This is the relation that would be predicted from the structure-factor calculations of a montmorillonite with a concentration of scattering power (three magnesium ions) in the octahedral position.

Figure 5 of Wyoming Bentonite I shows the reverse relation. The diffraction intensities near $\sin \theta/\lambda = 0.09$ are more intense than those at 0.15. This suggests less scattering power in the octahedral layer than in that of hectorite. The other two samples of Wyoming bentonite are more nearly alike, with both

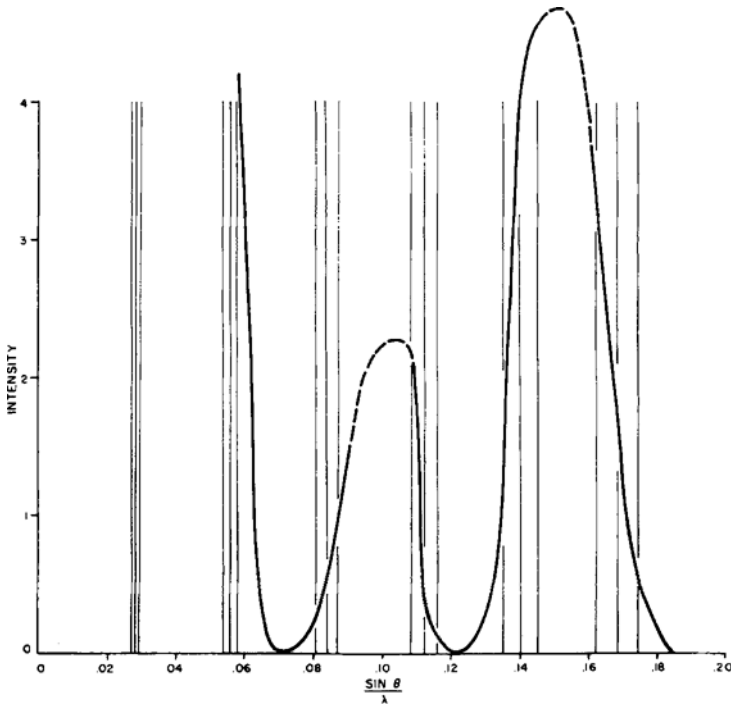


FIGURE 4.—Curve of adjusted observed diffraction intensity of hectorite-organic complexes.

intensity peaks being about the same height. The amplitudes of the peaks are somewhat less than those of Wyoming Bentonite I. It is suspected that this general reduction in intensity may be related to the degree of orientation of the particles in the flakes of Wyoming Bentonites II and III rather than the structure factor.

The asymmetry of the peak near 0.15 is particularly noticeable for Wyoming Bentonites II and III. There is a suggestion of an irregularity in the curve on the positive slope of this peak which is possibly an unresolved maximum. More closely spaced data will establish the importance of this suggestion. On the other hand, a reduction in the diffracting power within the tetrahedral layer may be responsible for an increase in diffraction intensity near $\sin \theta/\lambda = 0.14$.

Intensity data at low values of $\sin \theta/\lambda$ (less than 0.06) were closely grouped. Variations in the intensity curves could not be shown adequately by drawing the curves through only two sets of points and were therefore not attempted. As complexes with more widely varying periodicities are studied the intensity curves can be extended to lower θ/λ values.

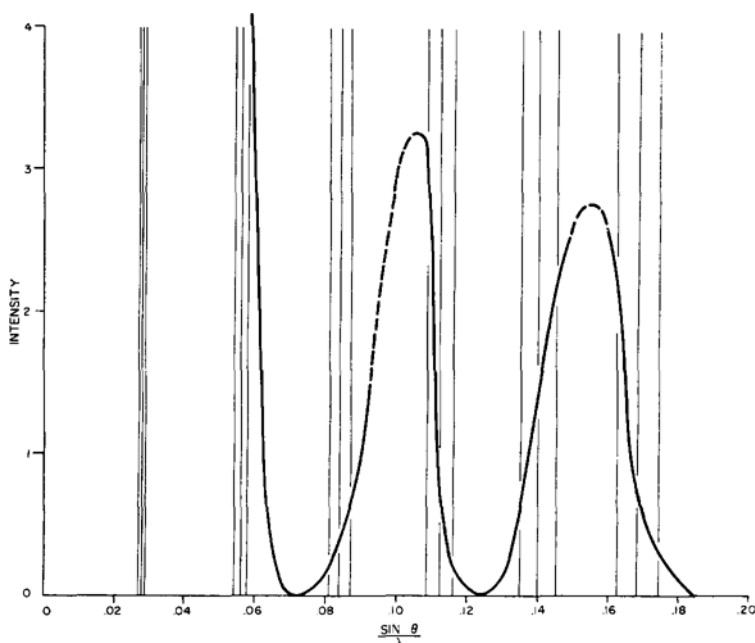


FIGURE 5.—Curve of the adjusted observed diffraction intensity of Wyoming Bentonite I-organic complexes.

SUMMARY

Diffraction intensity data from organic-montmorillonite complexes are difficult to interpret because of the unknown effect of the organic interlayer material. By drawing continuous intensity variation curves for several different montmorillonite samples a dependable determination of the organic contribution can be made. After this information has been gathered for a large number of organic liquids, it can be used as a means of identifying unknown organic complexing agents. More data will also be available to determine the way in which interlayer material, including water, is held.

The montmorillonite intensity variation curves shown in this report differ from one sample to another. A detailed analysis of the differences among the curves for a series of montmorillonites whose compositions are known will provide more information on the structure of montmorillonites. Intensity variations that cannot be justified by manipulation of the constituents that are shown to be present in the montmorillonite can be checked against possible crystal imperfections.

Intensity variation curves for montmorillonites in mixture with other minerals can be drawn using data for all orders except those that are modified by diffraction from the contaminant. All orders will be reduced in intensity by

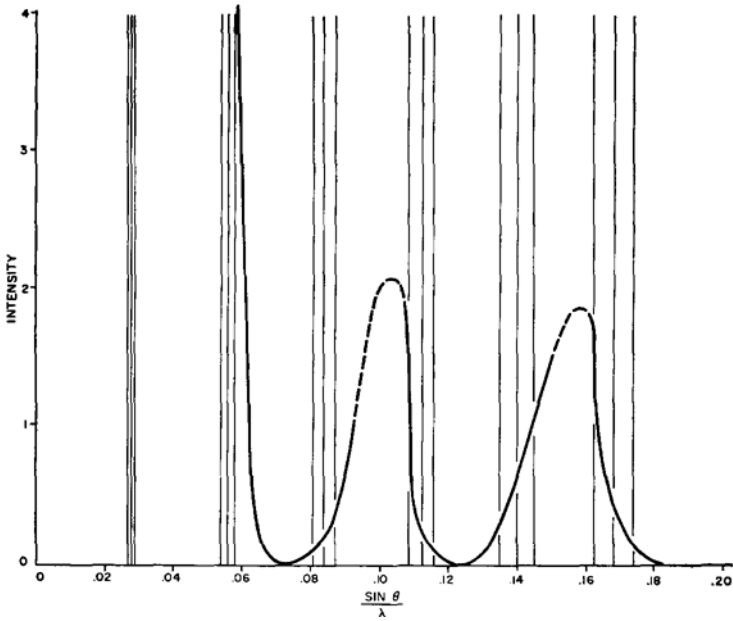


FIGURE 6.—Curve of the adjusted observed diffraction intensity of Wyoming Bentonite II-organic complexes.

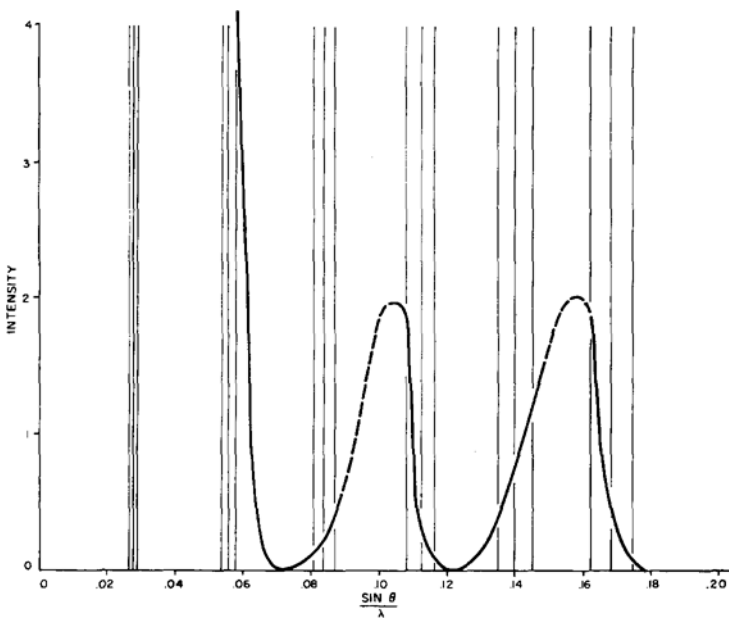


FIGURE 7.—Curve of adjusted observed diffraction intensity of Wyoming Bentonite III-organic complexes.

the dilution effect, but the curve will still be characteristic of the montmorillonite. Interlayer mixtures are more difficult to treat because of broad diffraction lines and coalescence of individual lines.

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