

AN X-RAY STUDY OF AN ETHYLENE GLYCOL-MONTMORILLONITE COMPLEX

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ABSTRACT

Oriented aggregates of ethylene glycol-montmorillonite were studied by x -ray diffractometer methods. Basal reflections, through the 00 14, provided the basis for structural analysis by Fourier and trial and error methods. On the basis of the intensity data, it is concluded that glycol molecules form a staggered, two-layered complex; water molecules and exchangeable cations lie close to but not coincident with a plane that separates the two glycol layers. The glycol molecules in each layer are disposed in c -axis face centered array. They are oriented so that the plane of symmetry of the aliphatic chain parallels the c -axis. The proposed structure is a two-layer modification of a previously described glycol-vermiculite structure.

INTRODUCTION

Bradley (1945) first applied the technique of one-dimensional Fourier synthesis to the study of organo-montmorillonite complexes. His work disclosed that ethylene glycol molecules form a two-layer sheet between the mica portions of the montmorillonite lattice. MacEwan (1948) studied the thicknesses, by x -ray methods, of the organic portions of a wide variety of organo-montmorillonite and organo-halloysite complexes. He concluded that the glycol molecules in each layer of the montmorillonite complex were oriented so that the plane of the zig-zag of the aliphatic chain lay parallel to the surface oxygen network of the interlamellar clay surface. MacEwan (1948) visualized the organic layer as a two-dimensional liquid without strict crystallographic regularity. Mackenzie (1948) showed that water molecules may proxy, to a certain extent, for glycol in a typical complex. Later studies by Brown (1950) indicated that the exchangeable cations lie along the center of the complex, *i.e.*, in the plane of symmetry.

This model of the glycol-montmorillonite complex has not been refined or modified by recent work. Most oriented montmorillonite aggregates produce no more than eight or nine basal reflections. Fourier syntheses based upon so few terms do not provide the requisite resolution for unique solutions of the positions and orientations of the glycol molecules.

In a recent paper, Bradley *et al.* (1963) have proposed a different structure for the glycol-vermiculite complex. A single crystal of vermiculite produced a sufficiently intense diffraction pattern to enable the recording of 16 orders of reflection. The $d(001)$ for the single-layer vermiculite complex is less than $d(001)$ for the two-layer montmorillonite complex; there-

fore, the d-spacings of the higher order terms are small enough to allow the resolution of the individual scattering centers within the glycol molecules. The structure proposed by Bradley *et al.* (1963) consists of glycol molecules oriented so that the plane of the zig-zag of the aliphatic chain is perpendicular to the basal oxygen sheet and parallel to the b-axis.

Experimental work described below indicates that a two-layer modification of a similar structure is probable for glycol-montmorillonite. Attempts to obtain close agreement between observed and calculated F factors, using MacEwan's model, have been unsuccessful.

Since the present paper was written, the author's attention has been drawn to an earlier paper by Brindley (1956) on the structure of the glycol-allevardite complex. Brindley suggested that the glycol molecules form a two-layer complex in which the planes containing the aliphatic chains lie parallel to the c-axis. The details of his Fourier projection in the interlamellar region are almost identical to those shown in Fig. 2 (of the present paper) for glycol-montmorillonite; apparently glycol-allevardite and glycol-montmorillonite complexes have similar or identical interlamellar structures.

LABORATORY PROCEDURES

Ethylene glycol-montmorillonite complexes were prepared from Clay Spur Bentonite (A.P.I. std. No. 26). The montmorillonite was dispersed in 0.01 N sodium pyrophosphate and settled to obtain a $<2 \mu$ (e.s.d.) fraction. The clay fraction was warmed in 0.05 N HCl (to remove iron oxides and carbonate), washed, and titrated with $\text{Ca}(\text{OH})_2$. The calcium saturated clay was washed to dispersion.

Oriented specimens for x-ray studies were prepared as follows. Portions of the dispersed montmorillonite were centrifuged on to glass slides. The method is similar to one described by Kinter and Diamond (1956). Four thin montmorillonite aggregates, $1\frac{3}{4} \times 1$ inches, were prepared in this fashion and dried at 110°C . No special precautions were taken to ensure complete water removal. The dried aggregates were then steeped in ethylene glycol (at 110°C .) until the transparent appearance of the specimen indicated glycol imbibition. The clay aggregates were peeled from the slides and carefully stacked, one on another, to produce a laminated specimen (Pézerat and Méring, 1954). The purpose of this procedure is to produce highly oriented specimens that exceed the requirements of infinite thickness for CuK_α radiation.

X-ray diffraction studies were performed using a General Electric XRD-5 spectrometer equipped with a copper tube. The radiation detector system utilizes a GE No. 6 proportional counter tube. This detector tube is linear to counting rates far in excess of any observed, therefore,

no correction was required for coincidence losses. Diffraction patterns were obtained using a 0.4° beam slit for the region between $2\theta = 5^\circ$ and $2\theta = 12^\circ$, a 1° beam slit between $2\theta = 10^\circ$ and $2\theta = 50^\circ$, and a 3° beam slit between $2\theta = 40^\circ$ and $2\theta = 90^\circ$. The use of these slits in conjunction with a $1\frac{3}{4}$ inch sample ensures that the beam width never exceeds the length of the sample (Klug and Alexander, 1954).

For the first eight orders, peak heights were scaled directly from the charts and considered to be proportional to peak intensities. The higher orders exhibited some peak broadening (probably due to imperfect $\text{CuK}\alpha_1 - \text{CuK}\alpha_2$ resolution); intensities for these reflections are based on peak areas. All peak intensities were put on the same basis by measuring several peaks, at the limits of each 2θ range, by the different methods and slits and calculating appropriate intensity conversion factors. Reproducibility studies on different specimens indicate a standard deviation of approximately 5% for the stronger peaks, and approximately 10% for the weaker ones (e.g., 00 11, 00 12, 00 13). For the very weak peaks (00 7 and 00 14) the standard deviation may be as great as 30%. A $d(001)$ value of 16.86 ± 0.01 was calculated from the seven highest orders.

METHODS OF CALCULATION

The method of structure analysis used here consists of the adjustment of trial structures toward optimum agreement between calculated F factors (F_c) and observed F factors ($|F_o|$). A General Electric 235 computer was used (1) to generate F_c values for different models of the montmorillonite-glycol complex, (2) to compute Fourier electron density projections, and (3) to compute Fourier difference syntheses (Cochran, 1951). Final adjustments of the various model parameters were made solely on the basis of closest agreement between $|F_o|$ and $|F_c|$. The refinement process consisted of minimizing the function

$$\sqrt{\sum |F_o - F_c|^2}$$

This method of structure analysis is much more time-consuming than straightforward interpretation of Fourier projections, but the ultimate attainable resolution is higher (Hughes, 1941). Furthermore, the method provides direct information on the degree to which various portions of the structure are resolvable. For example, if the trial structure contains atoms at a specific position in the unit cell, and the Fourier curve of F_c shows no electron maximum at that coordinate, then the investigator will not expect to observe the position of these atoms on the Fourier curve of F_o . Conversely, the method allows the rapid distinction between real electron maxima and termination-of-series ripples on the projections (Cochran, 1951). Peaks on the Fourier projection of F_c where no atoms

occur in the trial structure show that these maxima are spurious and can be disregarded on F_0 curves. The usual method for identifying termination-of-series ripples is to reduce F factors by an artificial temperature factor of the form $e^{-A \sin^2 \theta}$ (Klug and Alexander, 1954). This method does indeed remove spurious ripples, but it also seriously compromises the resolution of valid details of the structure (Cochran, 1951).

RESULTS

Table 1 summarizes the proposed model for the structure of glycol-montmorillonite. One-half of a unit cell is shown. The composition of the

TABLE 1. PROPOSED STRUCTURE FOR ETHYLENE GLYCOL-MONTMORILLONITE

Atomic Coordinates in Å	Atoms	Temperature Factor B, in Å ²
0	1.54 Al 0.16 Fe 0.33 Mg	1.68
1.06	4 O 2 OH	1.68
2.70	3 Si	1.68
3.27	6 O	1.68
6.12	1.70 H ₂ C-HO	11.0
7.07	1.70 CH ₂ -OH	11.0
7.94	0.80 H ₂ O 0.20 Ca	1.68

mica portion of the structure is taken from Kerr *et al.* (1950). The coordinates of the atoms in the mica portion of the lattice are modified from those listed by Pézerat and Méring (1954). Neutral atom scattering factors (Ibers, 1962) were used in all calculations, and the random powder Lorentz-polarization factor

$$\frac{1 + \cos^2 2\theta}{2 \sin^2 \theta \cos \theta}$$

was used in reducing all intensity data to $|F_0|$ factors.

Figure 1 shows a projection of the structure on to the bc plane. The glycol molecules have been positioned solely to rationalize volume re-

quirements with relative electron densities. The structure of the glycol molecules in the interlamellar space is simply a two-layer modification of the glycol-vermiculite structure (Bradley *et al.*, 1963). The glycol molecules are oriented with their plane of symmetry parallel to the bc plane (or along a 110 analog) in c -axis face-centered array. The second layer of glycol is displaced in the b direction, leading to a displacement of approximately $\frac{1}{2}$ an oxygen diameter between opposite oxygen networks of the

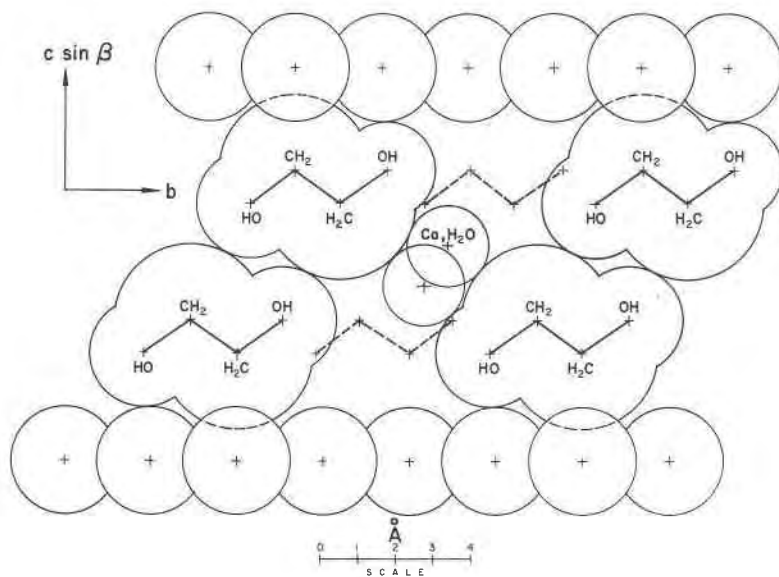


FIG. 1. Proposed structure of the glycol layer projected on to a plane parallel to bc . Water-calcium positions may be at either position shown at the center of the figure. Glycol molecules at the distance $a/2$ in front of and behind the plane of the projection are indicated by dashed aliphatic chains.

clay surface. An alternative situation involves displacements in both the a and b directions. The x -ray data do not allow the selection of the most appropriate of these stacking possibilities; quite arbitrarily, the former is assumed here.

Water molecules and exchangeable cations (up to the exchange capacity) occupy spaces between the two glycol sheets. These positions are close to, but not exactly coincident with the center of the complex. Actually, the available space would allow the H_2O , Ca to be anywhere between the two positions shown on Fig. 1, but the x -ray intensities agree better with a distribution of sites up and down against the OH groups of adjacent glycol molecules (Table 3). Figure 1 shows that the limiting di-

mension of the voids between glycol sheets is approximately 2\AA . Thus calcium ions fit well, but water molecules that act as rigid spheres with a radius similar to oxygen (*i.e.*, $\sim 1.4\text{\AA}$) can not be accommodated. However, it should be noted that slight adjustments in the relative displacement of the glycol sheets cause proportionately large increases in the limiting dimension of the voids. Furthermore, no account has been taken of the effects of polarization and hydrogen bonding, which would cause the water molecules to depart from spherical symmetry. In addition, only 3.4 out of four possible glycol positions appear to be occupied, indicating that somewhat more void space is available than that shown on Fig. 1. The present data, and the resulting analysis, are not sufficiently precise to evaluate these possibilities. Nevertheless, it is concluded here that the geometric limitations of the model do not preclude the occupancy of available voids by water molecules. There are two H_2O , Ca positions per unit cell. Proper adjustment of the calculated F factors requires that ions (or molecules) with scattering factors of ~ 10 (*e.g.*, H_2O , Na^+ , or $\frac{1}{2}\text{Ca}^{2+}$) occupy 2.4 such positions. This is in excess of the available positions. But, if the complex is assumed to contain 1.6 water molecules and 0.4 calcium ions per unit cell, then the required scattering power is approached without violating cation exchange capacity or steric limitations. Because all available spaces appear to be filled, the water molecules must occupy most of the positions, for if all of the positions were filled with calcium or sodium, the cation exchange capacity of the montmorillonite would be greatly exceeded.

The glycol-vermiculite structure (Bradley *et al.*, 1963) shows the filling of available sites near the van der Waals surface of the clay's oxygen network. These positions are apparently vacant in the present structure although steric considerations make them suitable for occupancy by exchangeable cations.

Table 2 shows a comparison between calculated F factors and intensities and observed F factors and intensities. $|F_o|$ values have been normalized on the basis of a minimum reliability factor; the intensities have been adjusted so that the strongest peak (001) is near 100.

The reliability factor (R) has been computed for the proposed model. This value is compared with other possible models (Table 3). The reliability factor is given by

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$$

The data of Table 3 show that variations of MacEwan's basic model are in poor agreement with observed F factors. The agreement is substantially better for the proposal structure. Furthermore, the data provide

TABLE 2. OBSERVED AND CALCULATED F FACTORS AND INTENSITIES FOR THE ETHYLENE GLYCOL-MONTMORILLONITE COMPLEX

	$ F_o $	F_c	I_o	I_c
001	63.4	+62.2	100	100
002	24.6	+23.2	3.7	3.43
003	36.2	-35.3	3.5	3.48
004	20.9	-20.8	0.65	0.66
005	70.9	+71.5	4.6	4.91
006	47.2	+45.7	1.4	1.35
007	8.5	- 6.8	0.032	0.021
008	38.7	-40.6	0.47	0.549
009	33.1	-34.9	0.27	0.308
00 10	3.6	- 6.0	N.D. ¹	0.0070
00 11	23.8	+24.2	0.09	0.090
00 12	24.2	+26.1	0.07	0.085
00 13	24.8	+23.2	0.06	0.056
00 14	17.6	+18.6	0.03	0.031

¹ Not detected; $|F_o|$ assumed to be one-half the minimum observable value (Buerger, 1960, p. 587).

some basis for locating the exchangeable cations and/or water at 7.94 Å instead of in the 180° plane (8.43 Å). The data of Table 3 indicate that the proposed model is to be preferred over MacEwan's. Reliability factors for structural models based on the single crystal Lorentz factor and/or lower temperature factors for the organic layer gave much higher values for R; therefore, they have not been considered here.

Figure 2 shows a one-dimensional Fourier electron density projection, and the final difference synthesis ($\rho_o - \rho_c$). The good agreement between F_o and F_c is shown by the low amplitude of the difference synthesis maxima and minima. At no position does the value for $\rho_o - \rho_c$ equal or exceed two electrons per Å, and the average deviation of $\rho_o - \rho_c$ about zero is ± 0.78 electrons per Å. These data refer to a unit cell containing ~ 500 electrons, whose formula is $2 \{Al_2Si_4O_{10}(OH)_2 \cdot 1.7(CH_2)_2(OH)_2 \cdot 0.8H_2O \cdot 0.2Ca\}$.

TABLE 3. A COMPARISON OF RELIABILITY FACTORS FOR SEVERAL STRUCTURAL MODELS

	0.4 Ca per Unit Cell, at 180°	1.6 H ₂ O, 0.4 Ca per Unit Cell at 180°	1.6 H ₂ O, 0.4 Ca per Unit Cell at 170°
Aliphatic Chain Flat (MacEwan, 1948)	0.211	0.198	—
Aliphatic Chain Upright	0.116	0.126	0.042

The ρ_0 curve of Fig. 2 shows several apparent discrepancies from the parameters of the proposed model. These may be listed as follows, (1) the electronic maxima are not coincident with the proposed atomic coordinates, (2) the second plane of the glycol molecules shows a lower electronic density than the first plane, and (3) the H₂O-Ca position is not resolved on the ρ_0 curve. These discrepancies occur to nearly the same degree on a Fourier projection based on F_c values. Consequently, the discrepancies probably arise from termination-of-series ripples or imper-

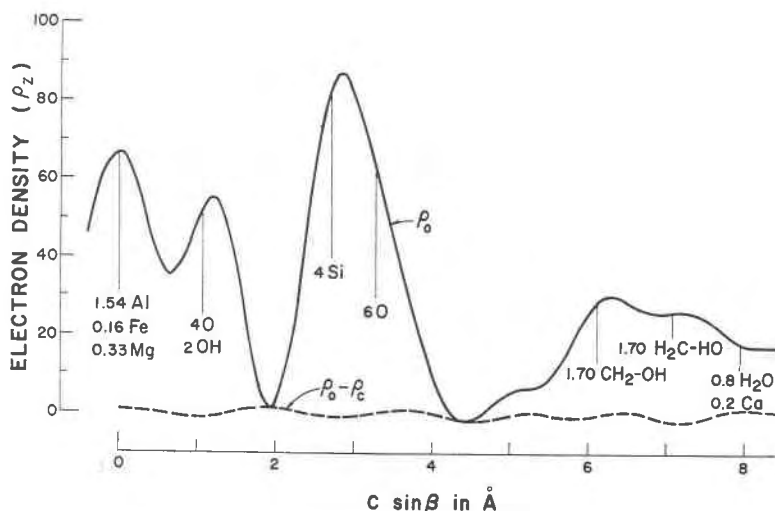


Fig. 2. One-dimensional Fourier synthesis of electron density parallel to $C \sin \beta (\rho_0)$. The curve labelled $\rho_0 - \rho_c$ shows the last difference synthesis.

fect resolution of the individual electronic maxima. This conclusion is, of course, predictable from the low amplitude of the $\rho_0 - \rho_c$ curve.

DISCUSSION OF MODEL PARAMETERS

The structural model developed above was determined empirically; each parameter was fixed solely on the basis of best agreement between $|F_o|$ and $|F_c|$. Such a procedure can lead to fortuitous agreement for models in which one gross error compensates for another. No rigorous and absolute verification can be accomplished here. Nevertheless, the validity of the proposed model is strengthened by evidence that the model parameters are within or close to limits that have been established by other workers on similar materials.

The temperature factors used are the most uncertain of the model parameters. Mathieson and Walker (1951) found a value of $B = 1.2 \text{ \AA}^2$

for the water-vermiculite complex. This value is somewhat different from the value used here ($B = 1.68 \text{ \AA}^2$). Atomic scattering factors for silicates, listed by Bragg and West (1929), show a decrease with increasing $\sin \theta/\lambda$ that roughly approximates a B value of 1.4 \AA^2 . This latter value is close to the one used here and suggests that $B = 1.68 \text{ \AA}^2$ may not be unrealistic.

Reasonable agreement between calculated and observed F -factors requires the application of a very high temperature coefficient ($B = 11 \text{ \AA}^2$) to the glycol scattering factors. This value greatly exceeds commonly used factors for organic crystals. Indeed, the magnitude of B used here calls for some explanation other than that of thermal vibration.

The high value for B can be explained by a totally different mechanism. If the glycol molecules (Fig. 1) are rotated slightly (clockwise) about an axis that parallels a and includes the center of gravity of each molecule, then the methylene and hydroxyl groups would be displaced from coplanarity. Each of the two planes shown in Fig. 1 would be split into a pair of closely spaced planes, producing an effect similar to that of a single plane affected by high amplitude thermal vibration. It may be that the rotations are random and are distributed so as to produce the effect of "frozen" thermal motion. However this alternative would randomize the positions of the water-calcium atoms; the non-anomalous B value for the water-calcium atoms seems to preclude this possibility. Consequently, it is suggested that the high value for the glycol temperature factor does not indicate thermal vibration, but instead, indicates a slight but consistent rotation of the glycol molecules; the rotation is in the plane of the projection of Fig. 1.

Bradley (1954, p. 329) has pointed out that no rigorous analysis has been made of the intensities of diffraction from oriented aggregates under the conditions of a focusing spectrometer. He found that the most reasonable results were obtained when the random powder (Debye-Scherrer) Lorentz factor was applied to intensity data. Schoen (1962) also found that the random powder Lorentz factor applied to oriented aggregates. On the other hand, MacEwan *et al.* (1961) maintain that a factor should be used that is intermediate between the random powder and the single crystal Lorentz factors. The writer has found that the use of the random powder Lorentz factor was necessary to obtain agreement between observed and calculated intensities for any acceptable model of the glycol-montmorillonite structure. As a further test, a comparison was made between calculated intensities and observed intensities from a dry sample of sodium Clay Spur montmorillonite. Calculated F factors were corrected for temperature (using $B = 1.68 \text{ \AA}^2$) and converted to intensities using both forms of the Lorentz-polarization factor. The results are

shown in Table 4. The agreement is good for intensities based on the random powder Lorentz factor. Intensities computed on the basis of the single crystal Lorentz factor show large deviations from observed intensities. It is concluded that *x*-ray diffractometer work on oriented clay aggregates requires the application of a factor that is very close to the random powder Lorentz-polarization factor.

MacEwan (1948) proposed a "flat" orientation for the glycol molecules because the interlamellar clear space just accommodates two molecular layers. The *a*-*b* area allows 1.75 molecules per layer per unit cell or 3.5 glycol molecules per unit cell. This figure is similar to the minimum amount of glycol required for a 17.0 Å *d*(001) spacing (Mackenzie, 1948).

TABLE 4. A COMPARISON BETWEEN OBSERVED INTENSITIES AND THOSE CALCULATED USING THE TWO FORMS OF THE LORENTZ-POLARIZATION FACTOR. DRY SODIUM CLAY SPUR MONTMORILLONITE; *d*(001)=9.7 Å

	<i>I</i> _{obs}	Random Powder	Single Crystal
		L-P <i>I</i> _{calc}	L-P <i>I</i> _{calc}
001	100	100	100
002	27.0	27.3	54.6
003	54.8	47.1	141.3
004	Not Detected	0.0002	0.0010
005	8.2	8.6	42.8

The glycol orientation proposed here also is consistent with the available interlamellar volume. The methylene groups of the glycol molecules seat into holes in the clay oxygen surface network (Bradley *et al.*, 1963). Two layers of glycol, offset as shown in Fig. 1, provide the correct thickness for a *d*(001) value of 16.9 or 17.0 Å, and the *a*-*b* area is sufficient for 1.70 molecules per unit cell per layer or 3.4 molecules per unit cell. Therefore, either model is satisfactory from a steric or stoichiometric point of view. The selection of the more appropriate of the two must be based on other considerations, *e.g.*, *x*-ray intensity data.

CONCLUSIONS

The model proposed here for the structure of the ethylene-glycol-montmorillonite complex gives calculated *F* factors that agree well with observed *F* factors. The random powder Lorentz factor has been shown to be applicable under the experimental conditions used. Temperature factors appear to be close to values established by other workers for similar systems, or can be explained by reasonable structural arrangements. The structure is consistent with steric and stoichiometric requirements. Con-

sidering all of the evidence, it is concluded that the organic layer of the glycol-montmorillonite complex contains 3.4 glycol molecules per unit cell, arranged in two layers; the glycol molecules are oriented so that their plane of symmetry parallels the b - c plane of the crystal; water molecules and exchangeable cations occupy positions just above and below an a - b plane that bisects the organic layer.

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