Research Report 171

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

by

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PREFACE

This paper was prepared by Dr. Robert C. Reynolds, Jr., Department of Geology, Dartmouth College. Dr. Reynolds is employed as an expert in conjunction with U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL) research project Physical Chemistry of Soil Water and Interfacial Phenomena During Freezing and Thawing (Materials Research Branch). The author wishes to express his thanks to Dr. E. H. McLaren whose comments concerning an original manuscript aided the author in a reinterpretation of some aspects of the structure. Dr. J. B. Lyons critically read the manuscript and contributed materially to its final form.

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SUMMARY

Oriented aggregates of ethylene glycol-montmorillonite were studied by X-ray spectrometric 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. This proposed structure is a two-layer modification of a previously described glycol-vermiculite structure.
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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; therefore, 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.

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 μ (e.s.d.) fraction. The clay fraction was warmed in 0.05 NHCl (to remove iron oxides and carbonate), washed, and titrated with Ca(OH)₂. The calcium-saturated clay was washed to dispersion.

Oriented specimens for X-ray studies were prepared as follows. Parts of the dispersed montmorillonite were centrifuged onto glass slides. The method is similar to one described by Kinter and Diamond (1956). Four thin montmorillonite aggregates 1 ½ x 1 in., 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 inhibition. The clay aggregates were peeled from the slides and
carefully stacked, one on another, to produce a laminated specimen (Pézerat and Mérin, 1954). The purpose of this procedure is to produce highly oriented specimens that exceed the requirements of infinite thickness for CuKα 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 $2\theta = 5°$ and $2\theta = 12°$, a 1° beam slit between $2\theta = 10°$ and $2\theta = 50°$, and a 3° beam slit between $2\theta = 40°$ and $2\theta = 90°$. The use of these slits in conjunction with a 1/4-in. sample ensures that the beam width never exceeds the length of the sample (Klug and Alexander, 1954, p. 229).

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 CuKα₁ - CuKα₂ resolution); intensities for these reflections are based on peak area. All peak intensities were put on the same basis by measuring several peaks at the limits of each $2\theta$ 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_0|). 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_0| and F_C. The refinement process consisted of minimizing the function

$$R^2 = \sqrt{\frac{\sum (F_0 - F_C)^2}{\sum |F_0|^2}}.$$  

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, p. 1742). 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_0. 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, p. 608). This method does indeed remove spurious ripples, but it also seriously compromises the resolution of valid details of the structure (Cochran, 1951).
RESULTS

Table I summarizes the proposed model for the structure of glycol-montmorillonite. One-half of a unit cell is shown. The composition of the mica portion of the structure is taken from Kerr et al. (1950, p. 53). The coordinates of the atoms in the mica portion of the lattice are modified from those listed by Pézerat and Mérig (1954). Neutral atom scattering factors (Ibers, 1962) were used in all calculations, and the random powder Lorentz-polarization factor

\[ \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \]

was used in reducing all intensity data to \(|F_0|\) factors.

Table I. Proposed structure for ethylene glycol-montmorillonite.

<table>
<thead>
<tr>
<th>Atomic coordinates in Å</th>
<th>Atoms</th>
<th>Temperature factor B, in Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.54 Al</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>0.16 Fe</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.33 Mg</td>
<td></td>
</tr>
<tr>
<td>1.06</td>
<td>4 O</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>2 OH</td>
<td></td>
</tr>
<tr>
<td>2.70</td>
<td>4 Si</td>
<td>1.68</td>
</tr>
<tr>
<td>3.27</td>
<td>6 O</td>
<td>1.68</td>
</tr>
<tr>
<td>6.12</td>
<td>1.70 H2C-HO</td>
<td>11.0</td>
</tr>
<tr>
<td>7.07</td>
<td>1.70 CH2-OH</td>
<td>11.0</td>
</tr>
<tr>
<td>7.94</td>
<td>0.80 H2O</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>0.20 Ca</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 shows a projection of the structure onto the bc plane. 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 one-half an oxygen diameter between opposite oxygen networks of the 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 H2O, Ca to be anywhere between the two positions shown on Figure 1, but the X-ray intensities agree better with a distribution of sites up and down against the OH groups of adjacent glycol molecules (see Table III). Figure 1 shows that the limiting dimension of the voids between glycol sheets is approximately 2Å. Thus calcium ions fit well, but water molecules that act as rigid spheres with a radius similar to oxygen (i.e., \(\sim1.4\)Å) 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 4
possible glycol positions appear to be occupied, indicating that somewhat more void space is available than that shown on Figure 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$_2$O, Ca positions per unit cell. Proper adjustment of the calculated F factors requires that ions (or molecules) with scattering factors of $\sim$10 (e.g., H$_2$O, Na$^+$, or $\frac{1}{2}$ Ca$^{++}$) 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 II shows a comparison between calculated and observed F factors and intensities. $|F_0|$ 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) computed for the proposed model is compared with other possible models (Table III). The reliability factor is given by
Table II. 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 |
| 010  | 3.6    | -6.0  | N.D.  | 0.0070|
| 011  | 23.8   | +24.2 | 0.09  | 0.090 |
| 012  | 24.2   | +26.1 | 0.07  | 0.085 |
| 013  | 24.8   | +23.2 | 0.06  | 0.056 |
| 014  | 17.6   | +18.6 | 0.03  | 0.031 |

Table III. Comparison of reliability factors for several structural models.

<table>
<thead>
<tr>
<th></th>
<th>$0.4 \text{ Ca per unit cell, at } 180^\circ$</th>
<th>$1.6 \text{ H}_2\text{O, 0.4 Ca per unit cell at } 180^\circ$</th>
<th>$1.6 \text{ H}_2\text{O, 0.4 Ca per unit cell at } 170^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic chain flat (MacEwan, 1948)</td>
<td>0.211</td>
<td>0.198</td>
<td></td>
</tr>
<tr>
<td>Aliphatic chain upright</td>
<td>0.116</td>
<td>0.126</td>
<td>0.042</td>
</tr>
</tbody>
</table>

$$R = \frac{\Sigma |F_o| - F_c}{\Sigma |F_o|}.$$  

The data of Table III show that variations of MacEwan's basic model are in poor agreement with observed $F$ factors. The agreement is substantially better for the proposed structure. Furthermore, the data provide some basis for locating the exchangeable cations and/or water at 7.94 Å instead of the 180° plane (8.43 Å). 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.

*Not detected; $|F_o|$ assumed to be one-half the minimum observable value (Buerger, 1960, p. 587).
Figure 2. One-dimensional Fourier synthesis of electron density parallel to \( C \sin \beta \). The curve labelled \( \rho_0 - \rho_C \) shows the last difference synthesis.

Figure 2 shows a one-dimensional Fourier electron density projection, and the final difference synthesis (\( \rho_0 - \rho_C \)). The good agreement between \( F_0 \) and \( F_C \) is shown by the low amplitude of the difference synthesis. At no position does the value for \( \rho_0 - \rho_C \) equal or exceed two electrons per Å, and the average deviation of \( \rho_0 - \rho_C \) about zero is ±0.78 electrons per Å. These data refer to a unit cell containing ~500 electrons, whose formula is \( 2 \{ Al_2Si_4O_10(OH)_2 \cdot 1.1CH_2O(OH)_2 \cdot 0.8H_2O \cdot 0.2Ca \} \).

The \( \rho_0 \) curve of Figure 2 shows several apparent discrepancies from the parameters of the proposed model: (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 \( H_2O-Ca \) position is not resolved on the \( \rho_0 \) 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 imperfect 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 \( F_0 \) 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 \( B = 1.2 \text{ Å}^2 \) for the water-vermiculite complex. This value is somewhat different from the value used here (\( B = 1.68 \text{ Å}^2 \)). 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 \( \text{ Å}^2 \). This latter value is close to the one used here and suggests that \( B = 1.68 \text{ Å}^2 \) may not be unrealistic.
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Reasonable agreement between calculated and observed $F$ factors requires the application of a very high temperature coefficient ($B = 11 \text{Å}^2$) 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 (see 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 Figure 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 Figure 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, p. 1391) also found that the random powder Lorentz factor applied to oriented aggregates. On the other hand, MacEwan, Amil, and Brown (1961, p. 408) 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, calculated and observed intensities from a dry sample of sodium Clay Spur montmorillonite were compared. Calculated $F$ factors were corrected for temperature (using $B = 1.68 \text{Å}^2$) and converted to intensities using both forms of the Lorentz-polarization factor (Table I V). 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). 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, p. 122). Two layers of glycol, offset as shown in Figure 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 features. The structure is consistent with steric and stoichiometric requirements. Considering 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; and water molecules and exchangeable cations occupy positions just above and below an a-b plane that bisects the organic layer.

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