

# CHARACTERIZATION OF MONTMORILLONITE SATURATED WITH SHORT-CHAIN AMINE CATIONS: 1. INTERPRETATION OF BASAL SPACING MEASUREMENTS

*by*

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## ABSTRACT

Basal spacing measurements were made for a montmorillonite saturated with a series of small aliphatic primary, secondary, and tertiary amine and quaternary ammonium cations, using wet, oven-dry, and glycerol-treated specimens. The spacings ranged from about 12 to 14 Å, depending on the cation, indicating that in each case a monolayer of cations is interleaved between adjacent montmorillonite layers. The observed spacings are consistent with the concept that the cations are oriented with their minimum thickness in the *c*-axis direction, but it is possible that the smallest cations have a long axis in this direction and are partially embedded in the clay surfaces.

Montmorillonite saturated with cations containing up to four carbon atoms retained some sensitivity to water, as indicated by a slight contraction of the lattice on oven drying and rapid re-expansion on exposure to the humidity of the laboratory atmosphere.

For cations having a layer thickness less than glycerol, limited lattice expansion occurred on glycerol treatment, usually to a spacing sufficient to accommodate a single layer of glycerol molecules. Apparently the cations function as pillars separating the montmorillonite layers, and the glycerol molecules may expand the lattice as necessary to enter the spaces between the pillars. However, exceptions occurred with methylamine-saturated montmorillonite, in which both one- and two-layer complexes of glycerol were present simultaneously in the same specimen, and with trimethylamine-saturated clay, in which two different one-layer complexes were present. It is suggested that the glycerol in one-layer montmorillonite complexes may exist in two orientations, one leading to a layer thickness of about 4.1 Å, the other to a thickness of about 4.6 Å.

## INTRODUCTION

The properties of montmorillonite saturated with large aliphatic amine cations have been studied fairly extensively in recent years, but relatively little work has been done with the smaller amine and quaternary ammonium cations. The present work represents an attempt to characterize the complexes formed on saturation of a montmorillonite with some of these smaller cations, particularly from the point of view of cation dimensions and packing of ions on the clay surface, and also to characterize the complexes formed by

glycerol with the amine-treated clays. This initial report is concerned with the determination of basal spacings of the various complexes, and the interpretation of the data in terms of the thickness and orientation of the cations and glycerol molecules.

### MATERIALS AND EXPERIMENTAL PROCEDURE

Volclay-brand Wyoming bentonite was used as a source of montmorillonite. The commercial product was fractionated by dispersion in water with sodium hexametaphosphate (Calgon) and sedimentation by centrifugation, the material coarser than the  $2\text{-}\mu$  size being discarded.

Amine cation-saturated specimens of the clay were prepared for X-ray diffraction using 1N solutions of the following amine compounds: methyl-, ethyl-, dimethyl-, diethyl-, di-*n*-propyl-, trimethyl-, triethyl-, tri-*n*-propyl-, and tri-*n*-butylamine hydrochloride, and also tetramethylammonium chloride and tetraethylammonium bromide. For each specimen an aliquot of the clay-water dispersion sufficient to yield about 100 mg of clay was used to prepare a thin film of clay as an oriented aggregate on a porous ceramic tile, by a centrifuge method described earlier (Kinter and Diamond, 1955). Saturation was accomplished by passing five separate 5-ml portions of the amine salt solution (fifty times the exchange capacity) through the clay film and tile held in a suction device described in the paper cited above. The clay film was then washed five times by passing 20-ml portions of distilled water through the film and tile in the same manner.

The solutions of the primary, secondary, and tertiary amine hydrochlorides were prepared by neutralizing the appropriate amine with concentrated hydrochloric acid and diluting to 1N with distilled water. Corresponding solutions containing the quaternary amine cations were prepared directly from the two salts, tetramethylammonium chloride and tetraethylammonium bromide. The amines and quaternary ammonium salts were Eastman Organic Reagents.

X-ray diffraction patterns were recorded with a General Electric XRD-3 diffractometer employing copper  $K\alpha$  radiation. Patterns were obtained for specimens in the following conditions:

- (a) wet, directly after the saturation and washing treatment described above;
- (b) air dried;
- (c) oven dried overnight at  $110^{\circ}\text{C}$ ;
- (d) after glycerol treatment.

The glycerol treatment involved application of an excess of glycerol to the clay film, placing the specimen over a supply of glycerol in a sealed container, and tempering overnight at  $70^{\circ}\text{C}$ . This tempering treatment yielded substantially the same basal spacings as treatment with glycerol alone, but it markedly improved the regularity of the sequence of basal reflections and greatly increased the intensity of the individual maxima.

## RESULTS AND DISCUSSION

*Wet Specimens*

Basal spacings of the wet amine-cation saturated specimens are listed in Table 1. The values given are averages calculated from several higher orders of reflection, and occupy a restricted range of 12.6–14.2 Å. For most specimens the X-ray maxima were surprisingly sharp and well defined, with a

TABLE 1.—BASAL SPACINGS OF WET AND OVEN-DRY AMINE-SATURATED MONTMORILLONITE

Cation	Basal spacings, Å		
	Wet specimens	Oven-dried specimens	Difference
Methylamine	12.6	12.16*	0.4
Ethylamine	12.94	12.66*	0.3
Dimethylamine	12.94	12.52*	0.4
Diethylamine	13.22	12.81*	0.4
Di- <i>n</i> -propylamine	13.28	13.15	0.1
Trimethylamine	13.5	12.84*	0.7
Triethylamine	13.40	13.26	0.1
Tri- <i>n</i> -propylamine	13.4	13.36	0
Tri- <i>n</i> -butylamine	13.6	13.51	0.1
Tetramethylamine	14†	13.85	†
Tetraethylamine	14.2	14.17	0

\* Averages of estimates based on higher orders of reflection, each order of reflection having been recorded individually immediately after a separate drying period.

† Diffuse nature of X-ray pattern of the second and higher orders precluded accurate estimation of basal spacing and of difference in spacing between wet and oven-dry specimens.

very regular sequence of reflections. This is in contrast to wet specimens of the same montmorillonite saturated with inorganic cations, which commonly exhibit only diffuse reflections lacking in higher orders. Since the basal spacing of the montmorillonite structure itself is 9.4 Å, and, according to Pauling (1940, p. 190), the thickness of a methyl group is about 4 Å, it is clear from the basal spacing values that no more than a monolayer of cations is present between adjacent montmorillonite layers.

*Air-dried Specimens*

Air drying of the wet amine-cation saturated specimens resulted in small reductions of about 0.1 Å in the basal spacings. Since the effect of air drying was so small and there was no control over the relative humidity, the basal spacing data for the air-dried specimens were not included in Table 1.

*Oven-dried Specimens*

The basal spacings observed after oven drying are also given in Table 1. In the normal X-raying procedure an oven-dried specimen was removed from the oven, mounted directly on the diffractometer, and the appropriate  $2\theta$  range ( $2^\circ$  to as high as  $60^\circ$ ) was covered in a continuous scan. This technique was satisfactory for the larger amine cations, but for the smaller ones rapid adsorption of water vapor from the atmosphere caused considerable expansion of the lattice to take place while the diffraction patterns were being recorded. Since appropriate accessory equipment was not available to prevent this adsorption and expansion during the X-raying, a special procedure to minimize the effect was adopted to record the patterns. The diffractometer was preset to within one-half degree of the expected position for a given maximum, the specimen was removed from the oven, mounted immediately in the diffractometer, and the maximum was recorded. The specimen was then returned to the oven to remove the small amount of moisture that had been adsorbed during the recording period, and the procedure was repeated to record the next order of reflection. For each recording, approximately  $1\frac{1}{2}$  min elapsed between the removal of the specimen from the oven and the recording of the maximum, the specimen remaining hot during this period. The basal spacing values for which this procedure was found necessary are indicated in Table 1. They were estimated from four or five individual higher orders of reflections which agreed within 0.05 Å for most specimens and within 0.10 Å in all cases. This regularity was comparable to that found with the larger cations by the normal continuous scan procedure.

The data in Table 1 indicate that with the smaller amine cations (up to four carbon atoms) the basal spacings are not fixed, but are from 0.3 to 0.7 Å higher for wet than for oven-dried specimens. It is clear that despite the amine saturation, water may still penetrate the interlayer spaces and slightly expand the lattice. On the other hand, saturation with cations containing six or more carbon atoms does result in virtually fixed basal spacings, the differences in spacings between wet and oven-dry specimens being not more than about 0.1 Å. These latter differences are consistent in direction, but are probably not much greater than the experimental error.

Jordan (1949) has shown that in the series of primary normal aliphatic amine cations, those up to decylamine yield one-layer complexes with montmorillonite, while dodecylamine and larger cations form two-layer complexes. There is little information in the literature concerning the size of cation at which a corresponding change takes place in the secondary or tertiary amine series. As discussed above, one-layer complexes were found in

the present work with the largest of the secondary and tertiary amine cations employed, di-*n*-propylamine and tri-*n*-butylamine. Although no further exploration was made in the secondary amine series, specimens saturated with the next higher member of the tertiary series, tri-*n*-amylamine, were examined and found to contain the two-layer complex, as evidenced by a basal spacing of approximately 18 Å.

Recently Rowland and Weiss (this Volume) reported that a two-layer complex of methylamine- or dimethylamine-saturated montmorillonite was obtained on treatment of Wyoming bentonite with concentrated solutions of methylamine and dimethylamine hydrochloride. However, as previously noted for these smallest two cations, clay treated as in the present study, i.e. by repeated leaching of a thin film of clay with an excess of 1N solution of the hydrochloride, formed only one-layer complexes. The effect was the same whether the clay film was X-rayed while still soaked with the amine hydrochloride solution, or after thorough washing with distilled water. Presumably, therefore, formation of a two-layer complex with methylamine or dimethylamine requires that the clay be in contact with a solution more concentrated than 1N.

So far as the writers know, there is little published information for comparison with the basal spacings observed here for the oven-dried specimens. Values generally 0.1 to 0.3 Å less than those reported here were cited by Barrer and Reay (1957) and Barrer and MacLeod (1955) for a montmorillonite that had been saturated with methylamine, dimethylamine, trimethylamine, tetramethylammonium and tetraethylammonium cations, all the specimens having been dried and outgassed under high vacuum. Greene-Kelley (1956) reported a value of 13.3 Å for both wet and air-dried specimens of a montmorillonite saturated with triethylamine cations, which is comparable to the 13.40 Å and 13.26 Å values reported here for a wet and an oven-dried specimen.

In discussing the basal spacings of clay-organic complexes, it has been customary to estimate the thickness of the organic layer by subtracting the theoretical thickness of the silicate layer (9.4 Å for montmorillonite) from the basal spacing measured by X-ray diffraction. MacEwan (1948) called this estimate of the thickness of the organic layer the "Δ-value". Δ-values calculated in this way for the several amine and quaternary ammonium cations used in this study are presented in Table 2. For comparison, corresponding values of minimum clearance thickness for the various cations were obtained by direct measurement of Fisher-Taylor-Hirschfelder atom models and are also presented in the table. In each case the Δ-value is somewhat smaller than the minimum clearance thickness measured from the model, the apparent contraction varying from 0.2 to 1.1 Å. Similar effects have been observed by a number of workers for adsorbed organic molecules as well as cations (Bradley, 1945; Greene-Kelley, 1955; Barrer and Reay, 1957). This apparent contraction of the organic layer has been variously ascribed to hydrogen bonding to the silicate surface, to partial keying into the silicate layer, or simply to compression exerted by the host montmorillonite lattice.

TABLE 2.—APPARENT CONTRACTION OF THE CATION LAYER IN AMINE-SATURATED MONTMORILLONITE

Cation	$\Delta$ -value Å*	Minimum clearance thickness value derived from model, Å	Apparent contraction, Å
Methylamine	2.8	3.7	0.9
Ethylamine	3.3	3.9	0.6
Dimethylamine	3.1	3.9	0.8
Diethylamine	3.4	3.9	0.5
Di- <i>n</i> -propylamine	3.7	3.9	0.2
Trimethylamine	3.4	4.5	1.1
Triethylamine	3.9	4.7	0.8
Tr- <i>n</i> -propylamine	4.0	4.8	0.8
Tri- <i>n</i> -butylamine	4.1	4.8	0.7
Tetramethylamine	4.5	5.3	0.8
Tetraethylamine	4.8	5.5	0.9

\* Observed basal spacing of oven-dried specimen minus 9.4 Å, the theoretical thickness of the montmorillonite layer.

Brindley and Hoffman (1962) have reviewed and discussed this subject in considerable detail.

In the foregoing discussion of the basal spacing and apparent contraction data, it has been assumed that the adsorbed ions are oriented so as to present their minimum thickness in the direction perpendicular to the layers. However, another interpretation is likely for the smallest amines, i.e. those containing only one or two carbon atoms. In a recent paper, Rowland and Weiss (this Volume) have suggested that when montmorillonite is treated with a relatively dilute solution of methyl- or dimethylamine hydrochloride, the adsorbed amine cations may be oriented with their long axis perpendicular to the silicate layers, the cations being partly embedded in the holes of the hexagonal oxygen rings of the silica sheets. The basal spacing values observed in the present work for these two, and also for the ethylamine cation, are consistent with either orientation, since the increased clearance thickness required for these cations in their vertical orientation could be compensated for by their being partly embedded in the 2.4 Å-deep oxygen-ring cavity. Evidence to be presented by the writers in a subsequent report in this series strongly supports the latter interpretation.

*Glycerol-treated Specimens*

Basal spacings observed for amine-saturated montmorillonite specimens treated with glycerol are given in Table 3. These spacings give no indication of the formation of two-layer complexes, except for methylamine. X-ray diffraction patterns of specimens saturated with this particular cation and then treated with glycerol, disclosed that both one- and two-layer complexes were present simultaneously. This simultaneous occurrence of the two types

TABLE 3.—COMPARISON OF BASAL SPACINGS FOR GLYCERATED AND OVEN-DRIED SPECIMENS OF AMINE-SATURATED MONTMORILLONITE, AND  $\Delta$ -VALUES FOR THE GLYCERATED SPECIMENS

Cation	Basal spacings, Å			$\Delta$ -value for glycerated specimens, Å
	Glycerated	Oven-dried	Difference	
Methylamine	13.60 and 18	12.16	1.44 and 6	4.2
Ethylamine	13.65	12.66	0.99	4.2
Dimethylamine	13.74	12.52	1.22	4.3
Diethylamine	13.40	12.81	0.59	4.0
Di- <i>n</i> -propylamine	13.40	13.15	0.25	4.0
Trimethylamine	13.99 and 13.6	12.84	1.16 and 0.8	4.6 and 4.2
Triethylamine	13.36	13.26	0.10	4.0
Tri- <i>n</i> -propylamine	13.47	13.36	0.11	4.1
Tri- <i>n</i> -butylamine	13.55	13.51	0.04	4.1
Tetramethylamine	13.96	13.85	0.11	4.6
Tetraethylamine	14.05	14.17	-0.12	4.6

of complex may possibly be due to inhomogeneity of the bentonite with respect to layer charge density; that portion of the material having lower charge density tending to expand more readily to admit two molecular layers of glycerol, and that of higher charge density tending to admit only one. Beavers and Larsen (1953) showed that a clay fraction of a Wyoming bentonite analyzed electrophoretically by schlieren moving boundary procedures behaved as though materials of two or more different charge densities were present.

The patterns of the glycerol-treated trimethylamine-saturated clay, although not showing the presence of a two-layer glycerol complex, were unusual in that they did show two distinct series of reflections indicating the simultaneous presence of two difference one-layer complexes—a predominant

one having a basal spacing very close to 14.0 Å, and another, representing only a small part of the clay, with a spacing of about 13.6 Å. This variation might also be accounted for by inhomogeneity of the montmorillonite with respect to layer charge density. The X-ray diffraction patterns for all the other cations showed only a single sequence of strong and well-ordered basal reflections, all for one-layer complexes. The basal spacing values cited in Table 3 are averages calculated from four or five individual higher orders of reflection. Agreement among the basal spacing estimates calculated from these individual orders of reflection is comparable to that previously cited for oven-dried specimens.

For comparison with the basal spacings of the glycerol-treated specimens, the corresponding values for oven-dried specimens are also given in Table 3. In general, the values from the glycerol treatment are higher, the amount varying with the size of the cation. With methylamine, the smallest cation, the spacing of the one-layer complex produced by the glycerol treatment is 13.6 Å, which is about 1.4 Å higher than the spacing for the oven-dried condition. For the other cations, differences between the spacings of the glycerol-treated and the corresponding oven-dried specimens decrease systematically with increasing size of cation, ranging from 1.2 Å for dimethylamine down to 0.1 Å or less for those cations having more than six carbon atoms. For the tetraethylammonium cation, the spacing of the glycerol-treated specimen was actually lower than that of the oven-dried specimen by 0.1 Å.

Delta-values for the glycerol-treated specimens are also given in Table 3. They may be placed in two groups, one whose values average 4.15 Å and one with values of 4.6 Å. MacEwen (1948) gave a  $\Delta$ -value of 8.3 Å for the two-layer glycerol complex, which corresponds to a thickness of 4.15 Å for the glycerol molecule. He also observed a lower  $\Delta$ -value of 3.8 Å for the one-layer glycerol complex of halloysite. In an earlier work Kinter and Diamond (1958) reported a one-layer glycerol complex of sodium-saturated montmorillonite which was obtained by heating the glycerol-treated clay. The basal spacing was 13.95 Å, which corresponds to a  $\Delta$ -value of 4.55 Å. Thus, the  $\Delta$ -values reported in Table 3 are within the range of previously reported estimates derived from glycerol complexes. Examination of an atom model of the glycerol molecule revealed that there are a large number of possible conformations and orientations of the molecule that can yield  $\Delta$ -values within this range. The fact that the experimental  $\Delta$ -values reported here fall into two distinct groups, and also that the two separate sequences of basal reflections found for one of the cations yielded a value in each of the two groups, suggests that two different orientations or conformations of the glycerol molecules are involved. The orientation leading to a  $\Delta$ -value of about 4.15 Å apparently corresponds to the state of the glycerol molecules in the normal two-layer glycerol complex, and that leading to the 4.6 Å value apparently corresponds to the orientation of the glycerol molecules found in the one-layer glycerol complex of sodium-saturated montmorillonite previously described.



Barrer and MacLeod (1955) and Barrer and Reay (1957) established the concept that in montmorillonite saturated with certain small amine cations, the cations act as "pillars" holding the individual montmorillonite layers apart to a spacing approximating the thickness of the individual cation. The pillars do not form a close-packed layer, and the interlayer space remaining between them is available for sorption of either polar or non-polar gases. These authors also established that further expansion of the basal spacing of the amine-saturated montmorillonite can accompany sorption of certain polar gases whose molecules require greater clearance space than that provided by the amine cation pillars.

The results for the sorption of glycerol in the present work are consistent with this "pillar" concept. For the smaller amine cations, penetration of glycerol molecules into the vacant interlayer spaces between the cation pillars is apparently accompanied by a lattice expansion to the clearance required to accommodate the glycerol molecules themselves. A mixed one-layer complex of glycerol molecules and amine cations thus may be said to be present. On the other hand, for the larger tertiary amine cations, interlayer separations established by the cations themselves approach the clearance required to accommodate glycerol molecules. Adsorption of a monolayer of glycerol molecules in the interpillar spaces, therefore, would require little, if any, expansion of the lattice. Since the changes in basal spacings for these cations were minimal, as indicated in Table 3, it is clear that not more than such a monolayer of glycerol molecules could have been adsorbed, but it is also not possible to decide unequivocally whether penetration of glycerol into the interpillar spaces has actually occurred. A similar uncertainty also applies for the quaternary ammonium cations.

In an earlier report Kinter and Diamond (1960) had interpreted similar X-ray data for glycerol-treated triethylammonium saturated montmorillonite to indicate that glycerol molecules do not penetrate between the unit layers. However, in view of the present results, it is now recognized that this interpretation is not necessarily correct. The problem of whether any such penetration actually does occur will be treated more fully in the next paper of this series.

## SUMMARY AND CONCLUSIONS

It has been shown that montmorillonite saturated with any of a number of short-chain normal primary, secondary, or tertiary amine or quaternary ammonium cations acquires a basal spacing characteristic of the formation of a complex consisting of a monolayer of cation "pillars" interleaved between adjacent montmorillonite layers. The basal spacing is generally quite regular, even with wet specimens, and is not significantly reduced by air drying. Oven drying results in slight contractions in spacing ranging from about 0.7 Å for the trimethylamine cation to about 0.1 Å or less for cations containing six or more carbon atoms. Upon re-exposure to the laboratory atmosphere, specimens that show significant contractions on oven drying undergo rapid partial re-expansion due to the sorption of water vapor.

Thicknesses of the cation layers estimated from basal spacing values were 0.2–1.1 Å smaller than minimum clearance thicknesses measured from atom models. One- and two-carbon amine cations may be present in other than minimum thickness orientation with respect to the basal plane, and, if so, they are partially embedded in the silica sheets.

The effect of glycerol treatment varied somewhat with the cation. For most of the smaller cations, basal spacings were obtained which are characteristic of the clearance thickness of a monolayer of glycerol molecules between the montmorillonite layers. However, with methylamine cations, at least part of the clay expands to admit two molecular layers of glycerol. This may be a reflection of the inhomogeneity of the Wyoming bentonite material, the fully expanding portion perhaps having a lower layer-charge density than the remainder. With trimethylamine-treated clay two distinct one-layer complexes of glycerol occurred simultaneously in the same specimen. This also may be an indication of the inhomogeneity of the montmorillonite.

In general, it is clear that for the smaller amine cations, glycerol penetrates the lattice and a complex consisting of cation pillars and interpillar glycerol molecules is formed in the interlayer spaces, with the separation between adjacent montmorillonite layers being controlled by the glycerol molecules. In most cases the orientation of the glycerol molecules apparently corresponds to that observed in the normal two-layer glycerol complexes of montmorillonite, which have a  $\Delta$ -value of about 4.15 Å per layer. Of the two one-layer glycerol complexes noted for trimethylamine, one gave a 4.2 Å  $\Delta$ -value, but the other 4.6 Å, apparently indicating two different orientations of the glycerol molecules. The 4.6 Å value corresponds to the orientation found in the one-layer glycerol complex previously reported for a sodium-saturated montmorillonite.

For the larger tertiary amine and quaternary ammonium cations, the observed changes in basal spacing on glycerol treatment were minimal, and it was not possible to decide unequivocally whether the lattice had actually been penetrated by glycerol molecules.

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